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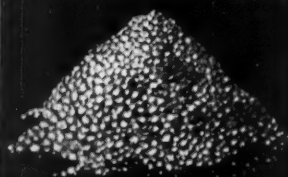
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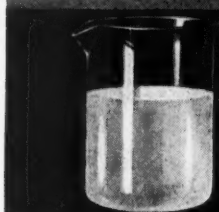
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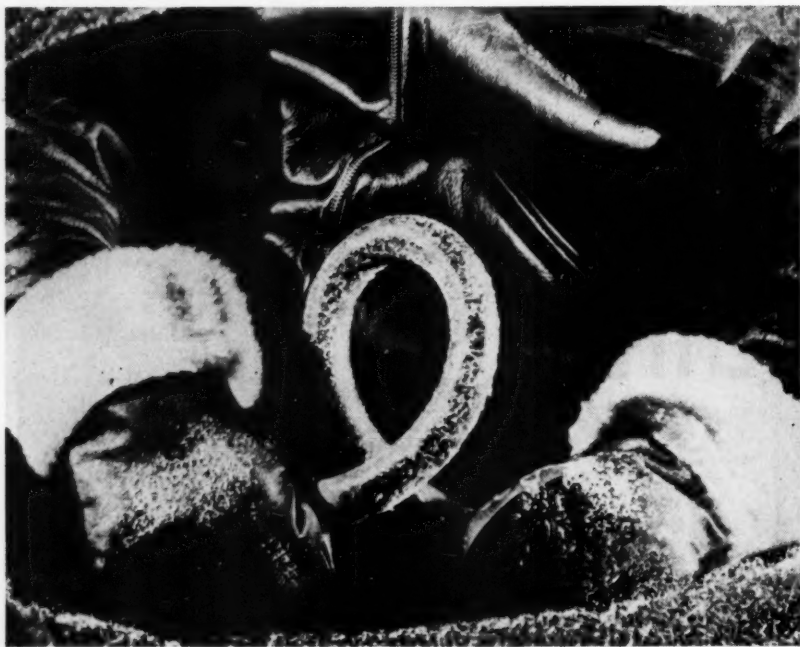
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long
did
it
take
to
get
from
here



Answer: Ten Years

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However, it was not until 1838, in England, that development work was begun on rubber insulation for electrical wires. By 1848, ten years later, vulcanization and an insulation compound had been developed, as well as a process for strip-covering wire with rubber. Thus, rubber insulation of electrical wiring was commercially practical. First production in the United States was started in 1868.

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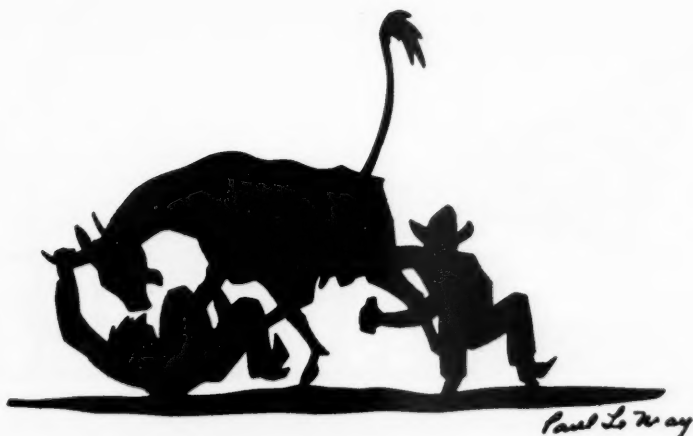
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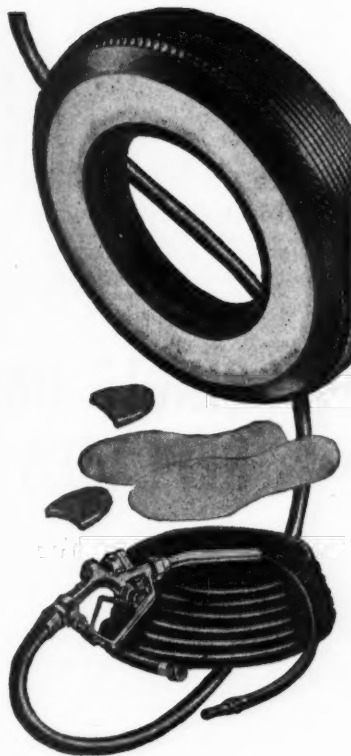
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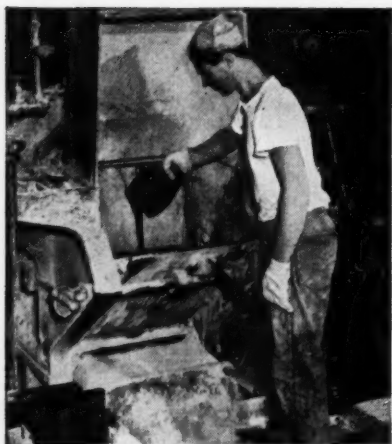
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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

HISTORY OF THE RUBBER INDUSTRY. Compiled under the auspices of the Institution of the Rubber Industry and edited by P. Schidrowitz and T. R. Dawson. W. Heffer & Sons Ltd., Cambridge, England. Cloth, 6 × 9 inches, 406 pages. 30s net. This is a genuine history, not a technical treatise. It was compiled under the auspices of the Institution of the Rubber Industry, and its impression on the reader is the masterly way in which the thirty-five authors, many of world-wide reputation, have shown to what extent our present scientific, technological, and commercial developments depend on the ideas and accomplishments of the past.

The thirty-five chapters deal with six general subjects: (1) origin of the rubber industry; (2) raw materials; (3) scientific and technical developments; (4) types of rubber products; (5) economic and social aspects of the industry, and (6) bibliographic information.

The reader will be struck by the impartiality of the authors. There is no attempt to "play up" British accomplishments, great as they are and much as they should be extolled; in fact, in some cases they seem almost to be underestimated. This is illustrated by the statement that Goodyear distinguished himself by recognizing the possibility of vulcanization, by working under conditions of extraordinary sacrifice, and by finally solving the problem of vulcanization, whereas Hancock made no such claim, and his personal narrative shows that such a claim could not have been supported. Surely, with respect to Hancock, this is a model of unsentimentality and impartiality, and by itself, it would leave the reader unaware of the accomplishments of this extraordinary man.

Of particular interest and value to many will be the bibliography of books and journals of the past and present, and a remarkable chronology of 330 important events, from B.C. to the present day; for example, seven in 1898 alone.

On the human side, one is touched by the succession of misfortunes; first that Fordyce Jones, editor-in-chief, and to whom concept of the book is due, lost by death one of his two collaborators, D. F. Twiss, an international figure, then himself had to relinquish the editorship to T. R. Dawson, who in turn died soon afterward. Fortunately the internationally renowned and beloved Dr. Schidrowitz had already taken the place of Dr. Twiss, and to him we owe completion of the book.

Finally, mention should be made of forty-four illustrations, some of great rarity and technical interest.

In brief, every rubber chemist and technologist should find something of interest and value in this book, just as he likes to browse through any other book on a subject close to his heart, which contains both familiar and unfamiliar facts skillfully and entertainingly presented. [From the *India Rubber World*.]

HANDBOOK OF MATERIAL TRADE NAMES: 1953. By O. T. Zimmerman and Irvin Lavine. Industrial Research Service, Masonic Bldg., Dover, N. H. 7½ × 10½ in. 794 pp. \$20.00, domestic; \$22.50, foreign.—The latest edition of

this handbook of trade names, the second to be published, is one of the finest what-how-who directories yet issued. It uses a large page size, double-column pages, large legible type, and has a durable binding. The 1953 edition is divided into three sections: (1) Alphabetical Listings, (2) Use Classification, and (3) Company Directory. The alphabetical listings include over 15,000 important trade name materials, ranging from abrasives to zeolites. For each material, data are furnished on physical and chemical properties, important industrial uses, and the name of the manufacturer or distributor. Symbols are used to indicate whether the material is a registered trade-mark, an unregistered trade-mark, or a generic or common name. The classification section is a new addition, and classifies all the materials described in the book according to their major uses or composition, thus making it possible to readily obtain information about specific types of materials. The directory section has been expanded so that it not only provides the address of each company whose products are in the book, but also lists the products described. The handbook should be of value to everyone who buys, sells, or develops new materials. [From *The Rubber Age* of New York.]

STANDARDS ON PLASTICS. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 705 pp. \$5.25 (in heavy paper cover).—This book gives a large number of standards, including specifications, definitions, and tests of a wide range of plastics. Most of the 135 standards have been developed through the work of ASTM Committee D-20 on Plastics. The committee for many years has been perfecting methods of testing, and those included are considered to be the best available. In addition to the standards of Committee D-20, a number are pertinent from other fields, including electrical insulation. The 27 specifications cover a wide range of molding compounds, such as phenolic, polystyrene, melamines, ureas, cellulose, acetates, vinyl chloride, methacrylate, and materials made from these compounds in the form of sheets, rods, tubes, and shapes. The large number of methods are arranged in the following classifications: strength properties; hardness properties; thermal properties; optical properties; permanence properties; analytical methods for plastics; molds and molding processes for plastics; conditioning of plastics; plates, sheets, tubes, rods, and molded materials; and electrical tests. Other section headings in the book include definitions and nomenclature, conditioning of plastics, miscellaneous subjects and appendixes. [From *The Rubber Age* of New York.]

SELECTED GOVERNMENT RESEARCH REPORTS. VOLUME I. PLASTICS. Issued by the British Ministry of Supply and published by Her Majesty's Stationery Office. American sales agents: British Information Services, 30 Rockefeller Plaza, New York 20, N. Y. Cloth, 6 × 9½ inches, 446 pages. Price, \$8.—This is a compilation of 21 reports selected from research on plastics under the direction of the British Ministries of Supply and Aircraft Production, now combined as the Ministry of Supply. The reports, prepared by both government, industrial, and university laboratories, were compiled by the Technical Information and Documents Unit of the Department of Scientific and Industrial Research. They are comprehensive and contain much previously unpublished information, but use of the book as a reference is handicapped by the lack of a subject index.

Titles of the reports are as follow: Mechanical Properties of High Polymers; The System Polymer/Plasticizer; Plasticizer/Polymer Interaction; Notes on the Sorption of Water by High Polymeric Materials; Linear Shrinkage of Phenolic Moldings During Post-Curing Stoving; Use of Flax Shives in Phenol-Formaldehyde Molding Powders; Effect of Fillers and Other Additions on the Elastic Modulus in Compression and on the Swelling of a Phenol-Formaldehyde Resin; Investigation Into the Setting Process of Phenol-Formaldehyde Resins; Note on the Ductility of Plastic Materials; Effect of Atmospheric Humidity on the Strength and Dimensions of Thermoplastics; Correction of the Indicated Impact Value of Brittle Plastics; Strength Tests of a Number of Similar Small Moldings in Phenol-Formaldehyde Synthetic Resin Molding Materials; Use of Reinforced Plastic Material in Aircraft Construction; Direction Strength and Stiffness of Fibrous Materials; Some Factors Influencing the Properties of Paper-Reinforced Synthetic Resin Sheet; Microscopic Examination of Reinforced Synthetic Resins; Strength of Bolted Joints in Perspex; Quantitative Method for Comparing Perspex Polishes; Synthetic Resin Glues (1) The Influence of pH on the Rate of Hardening of Cold-Setting Glues, and (2) Setting Time/pH Characteristics of Cold-Setting Resins Prepared From Some Monohydric Phenols; and Chemical Factors Involved in the Gluing of Wood With Cold-Setting Urea-Formaldehyde Resins—Failing Load of Gap Joints.—[From the *India Rubber World*.]

WRITING THE TECHNICAL REPORT. Third Edition. J. Raleigh Nelson. McGraw-Hill Book Co., Inc., 330 W. 42nd St., New York 36, N. Y. Cloth, 6 by 9 inches, 369 pages. Price, \$4.50.—In contrast to most books on technical writing which stress form and convention, this volume places major emphasis on basic principles and procedures, with the aim of developing proper attitudes and sound judgment. Since a report is planned for a specific use or purpose, it is the author's intention to aid the writer in grasping and evaluating the salient features of the problem which is the subject of the report. As such, the book will be of interest and value to students and professional men faced with the need of writing reports and similar communications.

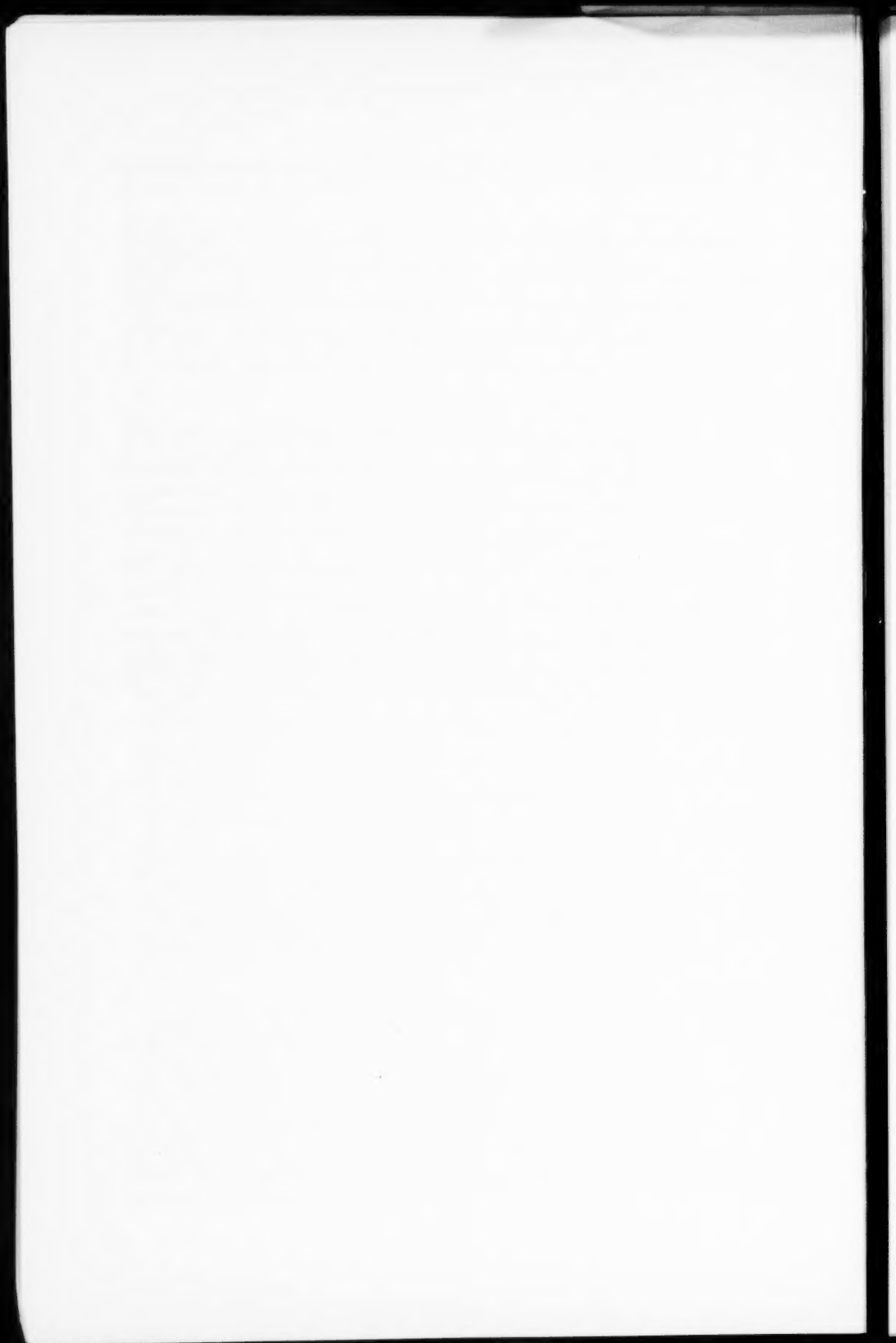
The book is divided into five sections. The first deals with the design and composition of the report. The second section gives specific directions for setting up reports, illustrated with annotated samples. A systematic procedure for the critical examination of the report appears in the following section, with clinical studies of typical cases. A summary of the fundamentals is presented in the fourth section, and the concluding section consists of a manual for report writing that can be used either as classroom or individual purposes. An adequate subject index is appended.—[From the *India Rubber World*.]

CHEMICAL PROCESS MACHINERY: 2ND EDITION. By E. Raymond Riegel. Reinhold Publishing Corp., 330 West 42nd St., New York, 36, N. Y. 6 × 9 in. 736 pp. \$12.50.—The first edition of this work was published in 1944 under the title of "Chemical Machinery". Because it was a show window for the remarkable resources of machinery and equipment designed, developed and, to a certain degree, perfected for services in the chemical industries, it met with instant favor and wide circulation. The new greatly enlarged edition brings the material of the previous volume abreast of latest developments, and scores of new diagrams, photographs, and tables make the construction and operation of recently employed machinery readily understandable to students and lay-

men as well as to engineers. As with the previous edition, the classification of the equipment by function gives the discussion a natural and logical organization.

Listing only equipment which is commercially available, the new edition describes and illustrates such new devices as multispheres and multicylinders, high-speed centrifugal separators, continuous crystallizers, absorption refrigerators, molecular stills, turbo-driers, etc. New material is included on distillation, the mixing of liquids, and instruments for the control of chemical processes. Expanded descriptions appear on evaporators, driers, heating and cooling equipment, pumps, and similar equipment. There are 27 chapters, three devoted to instrumentation, and a subject index. [From *The Rubber Age* of New York.]

CHEMISTRY . . . KEY TO BETTER LIVING. Compiled by the Staff. American Chemical Society, 1155 Sixteenth St., N.W., Washington 6, D. C. $9\frac{1}{4} \times 12$ in. 244 pp. \$4.00.—Issued in commemoration of the Diamond Jubilee of the American Chemical Society in 1951, and consisting of reproductions which originally appeared in both *Industrial and Engineering Chemistry* and *Chemical Engineering News*, this attractive volume reviews the development of chemical science and its industrial applications in a series of papers on chemical progress during the 75 years since the founding of the society. The part the society and its various divisions played in the advancement of chemical knowledge and skill during this period is emphasized. The section on "Rubber Chemistry" was furnished by R. P. Dinsmore, vice-president in charge of research, Goodyear Tire & Rubber Co. The volume should be a valuable reference in the libraries of industrial concerns, research laboratories, and educational institutions. [From *The Rubber Age* of New York.]



POLYURETHANES. IX. NEW TYPES OF HIGHLY ELASTIC PRODUCTS: VULCOLLANS.

PART 2 *

E. MÜLLER, O. BAYER, S. PETERSEN, H. F. PIEPENBRINK,
F. SCHMIDT, AND E. WEINBRENNER

MAIN SCIENTIFIC LABORATORY, FARBENFABRIK BAYER,
BAYERWERK, LEVERKUSEN, GERMANY

INTRODUCTION

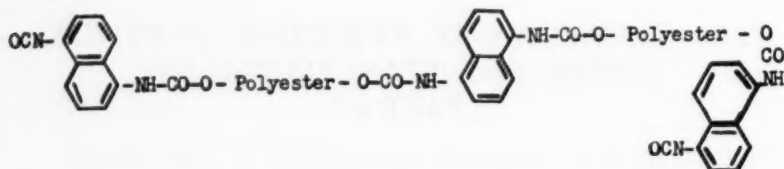
The polyesters which serve as raw materials for Vulcollan are of linear structure, with free hydroxyl groups on the chain ends. They have an average molecular weight of about 2000. The diisocyanate reacts first with the hydroxyl groups in such manner that several polyester chains are coupled together through urethane links. In general, about 30% excess of diisocyanate over the amount corresponding to the hydroxyl number of the polyester is used. Consequently, it appears that two to three polyester chains are linked into a macromolecule bearing free isocyanate end groups. This so-called chain lengthening to "isocyanate polyester" is followed by treatment with water, whereby further chain lengthening occurs through urea group formation, which is accompanied by evolution of CO₂ gas. Since the urea groups bear reactive hydrogens which in turn react with isocyanate, this is the point of attack for network formation. Thus, water functions both as chain extender and cross-linking agent. In summary, there are three distinct stages in the formation of the new products:

1. Preparation of the linear polyesters.
2. Chain lengthening to "isocyanate-polyester".
3. Urea formation with water and cross-linking, which have already been considered thoroughly¹.

Our further work dealt primarily with the cross-linking reaction; preparation of the linear polyester and chain lengthening to the isocyanate polyester were carried out as previously. The polyesters used for this study were prepared by thermal esterification of the glycols with dibasic acids, and were limited to polyethylene adipate, poly-1,2-propylene adipate and mixtures of these two esters. These two types were distinguished from all others by the good mechanical properties of the products obtained from them and were, therefore, selected for the following study. They differ from each other in that polyethylene adipate yields products most of which harden on long storage in the cold or even at room temperature, whereas poly-1,2-propylene adipate, or mixtures of ethylene and propylene adipate which contain at least 30 parts of the propylene polyester, give products which are completely stable toward cold and storage.

* Translated by (Miss) Leora Straka of the Goodyear Tire & Rubber Company, Akron, Ohio, from the *Angewandte Chemie*, Vol. 64, pages 523-531, October 7, 1952. Communication VIII of this series is by Höchtl, in *Kunststoffe* 40, 221-232 (1950), and deals with the synthesis of polyurethanes by the diisocyanate method and describes various products.

The chain-lengthening reaction was carried out with anhydrous ester and 1,5-naphthalenediisocyanate to yield an isocyanate polyester of the following structure:



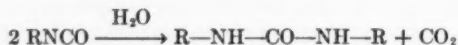
The proportions were usually so chosen that 2 to 3 polyester chains were bound together, which was done by using about a 30 per cent excess of isocyanate over the amount calculated from the OH number of the polyester.

The isocyanate polyester so obtained was now treated with the most diverse network-forming agents. First the cross-linking reaction of the isocyanate polyester with water will again be referred to.

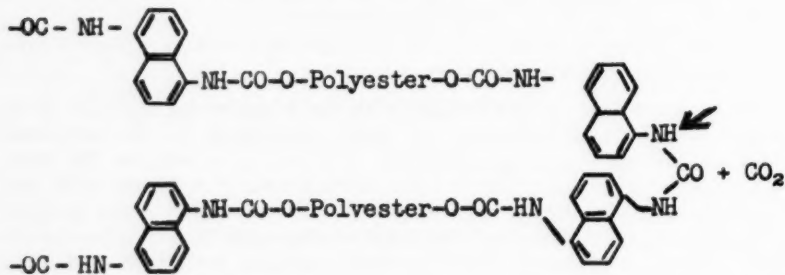
DISCUSSION OF VARIOUS CROSS-LINKING POSSIBILITIES FOR ISOCYANATE POLYESTERS

Water

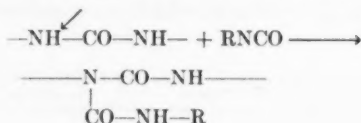
It is known that isocyanates react with water to form ureas and carbon dioxide:



The water couples two isocyanate molecules to a symmetrical urea, and thus behaves toward isocyanate as a bifunctional compound. With isocyanate polyester the water effects first a further chain coupling through urea groups, with simultaneous formation of CO_2 .



The hydrogen atoms of the urea group are now capable of reacting in turn with isocyanate polyester still present. Such reactions of low molecular weight disubstituted ureas with isocyanates are known. The reaction is as follows:



With polyesters containing isocyanate groups, the reaction furnishes cross-linking sites which lead to three dimensional supermolecules.

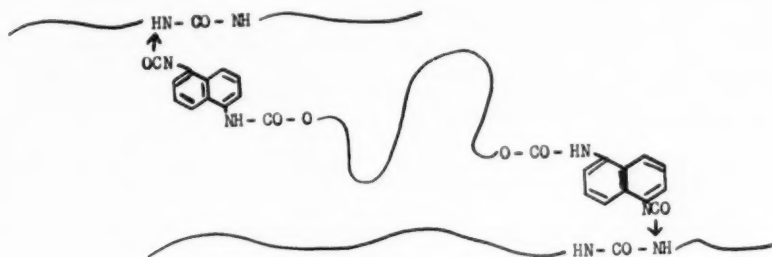


FIG. 1.

Hydrogen Sulfide

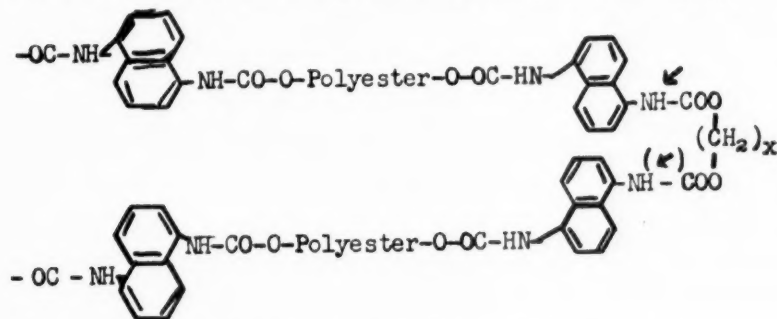
The use of hydrogen sulfide, the sulfur analog of water, was obvious. Hydrogen sulfide reacts with isocyanates to form symmetrical ureas and carbon oxysulfide².



The reaction takes the same course with isocyanate polyesters to give sulfur-free products which are identical to those obtained by cross-linking with water. Since the two are indistinguishable in composition, it is not surprising that the overall course of the reactions, as well as the physical properties of the products are identical. Since hydrogen sulfide offers no advantage over water cross-linking, it is without commercial significance because of the unpleasant properties of hydrogen sulfide.

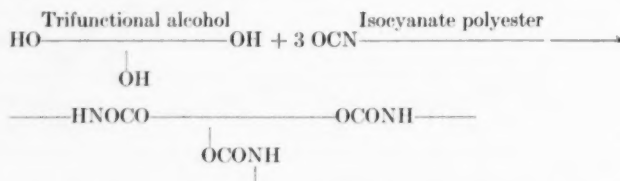
Glycols

It was now of interest to determine how other bifunctional compounds such as, for example, glycols behave toward the isocyanate polyesters. As was to be expected, a lengthening of the isocyanate polyesters occurred here also, not by way of the urea group, but through two closely adjacent urethane groups:

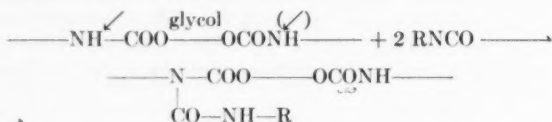


This stage of the reaction is associated with a certain increase of viscosity. If the proportions are so chosen that the glycol is present in deficiency or in amount nearly equivalent to the free isocyanate content of the isocyanate polyester, the

reaction does not stop at this stage, but leads gradually through a highly viscous condition to a crumbly insoluble material, which, by further processing gives valuable rubbery products. The course of the cross-linking reaction is at first not quite clear. From earlier work we knew that tri-functional alcohols when made to react with the isocyanate polyester gave cross-linked products which showed very poor tear resistance. In this type of structure there appear on the ends of each isocyanate-ester group cross-linking sites which are regularly distributed through the molecule:



With the use of bifunctional glycols this cross-linking site is not present and one must, therefore, be inclined toward the assumption that, analogous to the urea cross-linking, the hydrogen atoms of the adjacent urethane groups are susceptible to reaction with isocyanate groups. It remains undetermined as to whether one or both of the urethane groups enter into the reaction. Such reactions of low molecular weight substituted urethanes with isocyanates are known³. They proceed as follows:



Hence in the isocyanate-ester-glycol product the cross-linking site apparently lies in the newly formed urethane group.

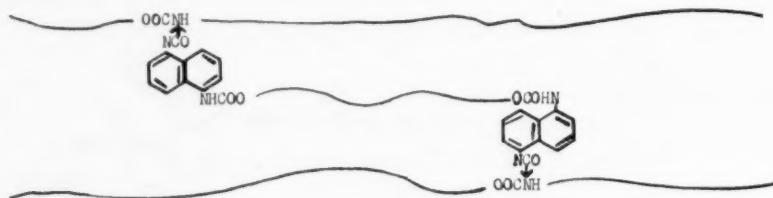


FIG. 2.

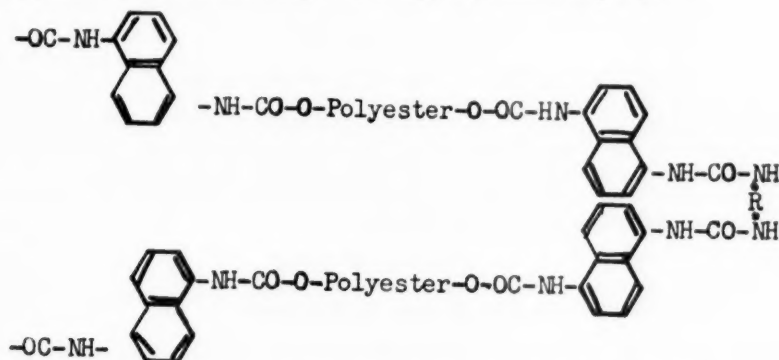
It is to be strongly emphasized that the overall glycol cross-linking process is possible only with reactive isocyanates, such as were designated earlier⁴ as "bulky and open".

Dithiols

If the oxygen in glycols is replaced by sulfur, the compounds are dithiols. These react similarly, although very slowly, to form thiourethanes. The reaction is too slow to be of practical significance.

Diamines

In the course of our work with new kinds of cross-linking agents, diamines were included. The idea was particularly obvious, since it is known that isocyanates react with amines to form symmetrically disubstituted ureas, the significance of which in water cross-linking we have already indicated. By treatment of isocyanate polyesters with diamines, coupling of the isocyanate polyester chains occurs through two closely adjacent urea groups:



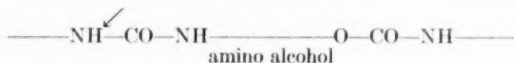
At the same time the excess of isocyanate groups reacts with the hydrogen atoms of the urea groups, whereby the cross-linking reaction takes place. The urea group thus furnishes the pivot point for cross-linking with diamine as well as with water cross-linking. An essential difference between the two lies in the fact that, with water coupling, two isocyanate polyester chains are linked through one urea group with formation of CO_2 , whereas the amine cross-linking proceeds by addition, and two isocyanate-polyester chains are coupled through two adjacent urea groups.



The amine cross-linking has great significance in the Vulcollan field, and in particular offers extensive possibilities for variation of the diisocyanate as well as the diamine. This will be discussed more fully in a following special section.

Amino Alcohols

Amino alcohols such as ethanolamine can be used instead of diamines as cross-linking agents. Here the coupling of two isocyanate polyester chains occurs through a urethane and a urea group which are closely adjacent.

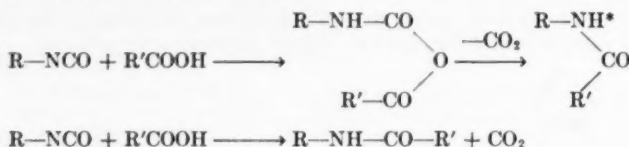


Apparently in this case urea cross-linking is the more ready reaction, and takes precedence over urethane cross-linking.

Dicarboxylic Acids

Lastly will be discussed the reaction of isocyanate esters with dicarboxylic acids, which also produces cross-linked products. According to the literature⁶,

isocyanates react with carboxylic acids to give mixed anhydrides of carboxylic and carbamic acids, which then split off CO_2 to form symmetrical disubstituted ureas. But immediate splitting of CO_2 can also occur, which leads to substituted amides. In both cases groups are formed which contain labile hydrogen atoms capable of reacting with isocyanate⁶.



Thus, if isocyanate polyester is treated with a dicarboxylic acid, such as maleic acid, coupling can occur through two adjacent urea or amide groups which in known manner react with excess isocyanate to establish cross-linking.

Thus in the formation of the new kinds of rubbery materials we can distinguish three basic kinds of cross-linking:

1. Cross-linking with water
2. Cross-linking with glycols
3. Cross-linking with diamines

Water cross-linking has been adequately discussed already. Glycol and diamine cross-linking will be given detailed consideration now.

CROSS-LINKING WITH GLYCOLS⁷

As already mentioned, the starting point is the chain-lengthened isocyanate ester. The lengthening was done primarily with 1,5-naphthalene diisocyanate, but its isomers, as well as diisocyanates of the biphenyl series, and especially those of the pyrene, fluorene and crysene series, are satisfactory for the reaction, whereas aliphatic and single-ring diisocyanates are suitable only under certain conditions.

The preparation is carried out as follows. First, the ester is carefully dried, whereby water is eliminated as a cross-linking agent, by melting at $120-130^\circ$ in a vacuum. The dried ester is then treated at 130° with the diisocyanate. The reaction is slightly exothermal and is over in a few minutes. The proportions are so chosen that normally 2-3 polyester chains are coupled together, which at an OH number of 50 requires the use of 15-16 per cent by weight of 1,5-naphthalene diisocyanate, based on the polyester. This isocyanate polyester makes a pourable melt, and is stable for several hours at elevated temperatures if protected from moisture. On very long heating or on storage of solutions, gelling due to cross-linking occurs in 1 to 2 weeks, even with most careful exclusion of moisture. This effect is evidently ascribable to the urethane groups present in the chain-lengthened isocyanate polyester, the hydrogen atoms of which react with the isocyanate groups in the manner indicated above.

The cross-linking of the isocyanate polyester proceeds very rapidly when a glycol such as 1,4-butanediol is added to the melt at about 130°C . After a few minutes a noticeable increase of viscosity occurs, and this finally proceeds through various intermediate stages to a crumbly material which can be milled to a cohesive sheet. The sheet can then be pressed as usual at $150-170^\circ \text{C}$ and about 700-2800 lbs. per sq. in. to the desired form.

TABLE I

Polyester	1,5-Naph- thane diiso- cyanate (%)	Cross-linking agent (%)	Tensile strength (lb. per sq. in.)	Elonga- tion at break (%)	Tear strength (lb. per sq. in.)	Rebound elasticity	300% Modulus (lb. per sq. in.)	Shore hardness
Polyethylene adipate, Hydroxyl number 50 70/30 Mixture*	16	2% Butanediol	4840	700	2130	59	1050	84
Polypropylene adipate	16	2% Butanediol	3980	680	1780	57	700	75
Polyethylene adipate	16	2% Butanediol	3190	830	1070	43	850	76
Polyethylene adipate	16	2.2% 1,4-Cyclo- hexane diol	5460	600	2490	59	500	67
Polypropylene/polyethylene adipates at 70/30	16	2.2% 1,4-Cyclo- hexane diol	4050	623	1590	58	780	75
Polypropylene adipate	16	2.2% 1,4-Cyclo- hexane diol	2630	720	1370	70	640	70
Polyethylene adipate	16	2.2% Thiodi- ethyleneglycol	3400	545	1780	69	480	62
Polypropylene adipate	16	2.2% Thiodi- ethyleneglycol	2490	715	1070	45	1220	74
Polypropylene adipate	16	2% Butanediol	4550	640	2260	70	500	60
Polypropylene adipate	16	2.5% Triethylen- glycol	2250	925	534	41	310	68
Polypropylene adipate	16	2.2% Dimethyl propyleneglycol	3130	780	590	41	360	62
Polypropylene adipate	16	2% Glycerol mono- phenyl ether	2630	900	534	33	870	—
Polyethylene adipate	16	2.2% 1,2-Cyclo- hexane diol	4980	777	2130	52	330	57

* The term "70/30 (or 60/40) Mixture" in this and the following tables indicates that a mixture of 70 (or 60) parts of polyethylene adipate and 30 (or 40) parts of polypropylene adipate was used.

Various types of glycols can be used as cross-linking agents, including aliphatic, cycloaliphatic, aromatic, and unsaturated glycols. Thus, in contrast to water cross-linking, there is an abundance of compounds which can function as cross-linking agents. Since each glycol influences the properties of the end product in some manner, it is possible to prepare rubbery products with various kinds of properties. The starting point for our investigations was butynediol:



from which products were obtained which were identical in properties with the water-cross-linked materials. Butenediol behaved similarly, so that our earliest work on the cross-linking reaction was done with unsaturated compounds. We found in the course of further work that saturated chloroglycols such as glycerol- α -chlorophydrin:



can be used. Finally it was established that the simplest member of the series, ethyleneglycol, though not particularly good, can also be used. Very good products were also obtained with butanediol. These were equivalent in proper-

TABLE II

Polyester	1,5-Naphthalene diisocyanate	1,4-Cyclohexanediol	Excess, diisocyanate (%)	Tensile strength (lb. per sq. in.)	Tear strength (lb. per sq. in.)	Permanent set (%)
Polyethylene adipate (Hydroxyl number 50)	15.4%	3.37	0.0	1660	590	48
Polyethylene adipate (Hydroxyl number 50)	15.4	3.09	0.5	1560	474	34
Polyethylene adipate (Hydroxyl number 50)	15.4	2.81	1.0	1910	1130	15
Polyethylene adipate (Hydroxyl number 50)	15.4	2.22	2.05	4840	2630	9
Polyethylene adipate (Hydroxyl number 50)	15.4	1.68	3.05	4580	2320	6
Polyethylene adipate (Hydroxyl number 50)	15.4	0.84	4.56	—	blown	—

ties to the water-cross-linked materials, whereas, with di- or triethyleneglycol decidedly soft products of lower modulus were obtained. Likewise, monoethers of glycerol, as well as sulfur-containing glycols such as thiodiethyleneglycol, proved to be usable. Cyclic glycols such as 1,4-cyclohexanediol or cathechol⁸ which contain two secondary hydroxyl groups were particularly suitable. Even glycols with tertiary hydroxyl groups, such as pinacol, were used with success. Table I summarizes the cross-linking reactions with various kinds of glycols and the physical properties so obtained.

The amount of glycol must be so controlled that there are not enough hydroxyl groups present to be stoichiometrically equivalent to the isocyanate groups. That is, there must be a certain excess of isocyanate present in every case. With an excess of glycol, products are obtained which are thermoplastic and of higher elongation. With decreasing amounts of glycol, the physical properties of the condensation product improve at first, until finally, beyond a certain isocyanate content, side reactions set in. These latter are apparently reactions of isocyanate groups with each other. They are characterized by gas

formation (blowing) and by decline of physical properties. Table II illustrates the influence of amount of cross-linking agent on physical properties.

1,4-Cyclohexanediol was used as the cross-linking agent. The polyethylene adipate used had a hydroxyl content of 1.5 per cent (OH number of 50). The quantity of 1,5-naphthalene diisocyanate calculated to be equivalent to 100 grams of polyester amounted to 9.3 grams; 15.4 grams was used. Thus, the excess of 1,5-naphthalene diisocyanate amounted to 6.1 grams. This excess of 6.1 grams of diisocyanate is equivalent to 3.37 grams of 1,4-cyclohexanediol. In Table II the amount of 1,4-cyclohexanediol was reduced stepwise, whereby the number of excess isocyanate groups increased proportionately.

The most favorable conditions thus lie in the range of about 2.05 per cent excess of 1,5-naphthalene diisocyanate over the bound cross-linking agent.

Since various glycols have different reactivities toward the isocyanate polyester, it is possible thereby to vary over a wide range the rate at which the reaction proceeds through the intermediate stages. Thus, 1,4-cyclohexanediol, with two secondary hydroxyl groups, reacts significantly more slowly than 1,4-butanediol. The retarding of the reaction is of great importance in processing. The more slowly the condensation proceeds through the intermediate stages, the longer the processing time. We therefore tried to regulate the condensation rate so that it could be adjusted to the desired processing technique. Reactivity of the isocyanate toward the polyesters as well as the glycols is involved. A significant retarding of the reactivity of the isocyanate group can be achieved by adding a small amount of acid substances to the polyester prior to its reaction with the diisocyanate. First of all, hydrogen chloride is mentioned, which can be added either as gas or in the form of hydrochloric acid. Similar effects are obtained from sulfur dioxide and boric acid, as well as organic acids present from the polyester preparation or by later addition. Also, compounds are suitable which are thermally decomposed into acidic substances, such as butadiene sulfone, which dissociates into butadiene and sulfur dioxide. A retarding effect can also be obtained from fillers of an acidic character, such as "A-Kohle", which is prepared under acid conditions.

Under certain conditions an acceleration of the reaction may be desired. This can be accomplished by stirring tertiary organic bases into the melt after the glycol addition. Tertiary amines such as hexahydrodimethylaniline, methylpiperidine, dimethylpiperazine, tribenzylamine, and tetramethyldiaminodipropyl ether are particularly effective. These catalysts are effective at concentrations as low as 0.001 per cent by weight of the polyester.

The reactivity of the commercially prepared polyesters toward the diisocyanates was quite erratic. This effect is apparently due to minor impurities which have a catalytic influence on the diisocyanate reaction. However, esters of equivalent reactivity are obtained by washing with water or an immiscible organic solvent such as benzene, or by blowing air or nitrogen through the melt at about 130° C until the desired reactivity of the polyester is reached. In many instances it is desirable for processing to combine these effects which influence reactivity; for example, by first retarding the reaction of the polyester with the diisocyanate by addition of a small amount of acidic material so that a stable fluid is obtained, and later accelerating the reaction again by addition of a basic catalyst.

PROCESSING THE REACTION PRODUCT

The prime significance of glycol cross-linking in combination with repression and acceleration of the reaction lies in the fact that new procedures for process-

ing are thus available. This is especially clear by comparison of glycol cross-linking with water cross-linking. Both kinds of curing start with the viscous pourable isocyanate-ester, which, when treated with water evolves CO_2 , and is transformed in a few minutes to a crumbly material which can be molded only under pressure. However, if the water is replaced by glycol, the condensation proceeds gradually through intermediate stages from viscous and pourable to a rubberlike condition. In contrast to the water cross-linking, no gas formation occurs. Therein lie the requisite conditions for a liquid phase processing without the aid of solvents. Consequently, new and formerly unavailable rubber processing techniques are possible, such as pouring the reaction mixture into the mold. The procedures described for water cross-linking allow the pouring of only the thinnest films, whereby the carbon dioxide formed by the effect of atmospheric moisture can escape without causing blowing. The pouring of unblown massive pieces would be possible by this procedure only if the carbon dioxide were pulled out by vacuum or were dissolved in the mixture by use of pressure. However, there are some instances in which blowing cannot be prevented, such as when pressure cannot be used or when the carbon dioxide cannot escape. In contrast to this, the glycol cross-linking technique allows the pouring of massive bodies of any desired thickness without the use of pressure. The procedure is as follows. The isocyanate polyester is treated at 130° with a deficiency of glycol with respect to the isocyanate content. After thorough mixing, the mixture is poured, while hot and before completion of the condensation, into the desired mold. For easy removal of the cured object, the mold is coated with a protective film, which may consist of waxlike materials or silicone resins. The reaction mixture is left in the mold at $100\text{--}120^\circ\text{C}$ until it has set. Then the piece is taken out and heated 10 to 15 hours at 100°C , whereby the cross-linking reaction proceeds to completion.

A special casting technique is centrifugal casting, whereby the fluid condensation product is poured into a rotating mold and remains in the mold with continued rotation until set. In this way bicycle or automobile tires with and without fabric or metal cords can be made.

Pressure-formed items can also be prepared by the glycol cross-linking procedure. In this case the condensation is carried to the point where the increasingly viscous mass finally becomes crumbly. For this procedure a mechanical mixer is useful. The crumbly product is then sheeted out on the mill and can be formed in a press at $125\text{--}150^\circ\text{C}$ to all kinds of molded objects. The pressed and cast products are identical in their physical properties.

The cast-press technique is a combination of the two processes. It differs from the casting technique in that, instead of pouring immediately after addition of glycol, the product is stored at room temperature. Since the cross-linking reaction practically stops on cooling, the products are still thermoplastic and can be stored several days in this condition. They can then be formed as desired by the conditions described for the press process. They show the usual physical properties.

Extrusion and calendering are also possible within the scope of glycol cross-linking. For these purposes it is necessary to carry the condensation of the isocyanate ester with the selected glycol to a stage intermediate between those used for casting and for pressing.

Preparation of the stock includes the following variations. Several per cent of hard paraffin or wax is added to prevent sticking to the roll. During condensation, the temperature is kept lower than that for the preparation of stock

for pressing. Addition of fillers such as carbon black, titanium dioxide, or silica chalk improves the processing of these materials. There is thus obtained a plastic material which at a temperature range of preferably 40–100° C can be formed in a conventional extruder into threads, strips, or tubes. In addition, thin sheets can be prepared by calendaring. To complete the reaction, these articles are subsequently heated as usual. It is best to cure after a short aging period. Toughness and gas impermeability are noteworthy as particularly valuable properties of the films and tubes obtained in this manner.

The materials obtained by the various processes for glycol cross-linking or variations thereof can be reprocessed in a simple manner. The old stock can be readily ground on the mill to a new sheet. Sheetting and especially later processing are facilitated by addition of softeners or of the chain-extended isocyanate polyester. In this way pressed articles can be made which retain 70 to 80 per cent of the physical properties of the original products.

CROSS-LINKING WITH DIAMINES*

The basic principle of amine cross-linking consists, as already mentioned, of treatment of isocyanate-esters with diamines. This reaction was carried out soon after the reaction mechanism of water cross-linking became known, but at first did not lead to the desired result. The reason for this was that the high reaction rate of isocyanate ester with diamines made impossible simple processing, even by the press process. Products were obtained which were generally non-homogeneous and which had poor physical properties. The reaction of 1,5-naphthalene diisocyanate-lengthened polyester with hexamethylenediamine proceeds practically spontaneously, and leads to inhomogeneous precondensate which cannot be molded under pressure without difficulty. We were, therefore, faced with the problem of retarding the reaction in such a manner that, as with the glycol cross-linking process, gradual transition through a series of intermediate stages from viscous to rubbery would occur. The retarding reactions described for the glycol cross-linking were not usable here, since the acidic retarders were neutralized on addition of the diamine.

In the course of our further work we noticed that the reaction rate was markedly affected by the basicity of the diamine. After changing from aliphatic to aromatic diamines we established that those compounds whose basicity is reduced by the introduction of negative substituents are particularly suitable. 3,3'-Dichlorobenzidine is an example of such a compound.

Further work showed that also by means of appropriate balance of the reactivities of the diamine and the diisocyanate, a gradual transition through the intermediate stages of the condensation is assured. This balance is easily possible, since the diisocyanates vary widely in their reactivity and the diamines vary in basicity. It is known, for instance, that aliphatic diisocyanates react more sluggishly than aromatic ones. Even among aromatic diisocyanates there are wide variations. Thus, 1,5-naphthalene diisocyanate is highly reactive, but the reactivity decreases regularly from this level in the series nitrobiphenyl diisocyanate, tolylene diisocyanate, hexamethylene diisocyanate. In the diamine series the behavior is the reverse; here, the aliphatic compounds are very much more reactive than the aromatic. As already mentioned, in the aromatic series considerable variation is achieved by the influence of negative substituents.

In order to satisfy the above-mentioned condition of a gradual transition through intermediate stages of the condensation, it is necessary to use a com-

TABLE III

Polyester	Castable combinations	Diamine	Tensile strength (lb. per sq. in.)	Elongation at break	Tear strength (lb. per sq. in.)	Rebound elasticity	300% Modulus (lb. per sq. in.)	Shore hardness
Polyethylene adipate, OH Number 50	Diisocyanate							
	1,5-Naphthalene, 16%	<i>o</i> -Dichlorobenzidine, 5.4%	3010	271%	2810	53	1510	80
Polypropylene adipate, 70/30 Mixture*	1,5-Naphthalene, 16%	<i>o</i> -Dichlorobenzidine, 5.4%	1190	463	1020	40	940	77
Polyethylene adipate	1,5-Naphthalene, 16%	<i>o</i> -Dichlorobenzidine, 5.4%	3030	600	1490	50	1020	80
	1,5-Naphthalene, 16%	<i>m</i> -Dichlorobenzidine, 5.4%	2450	533	1920	45	340	59
70/30 Mixture*	Toluene, 13%	<i>o</i> -Dichlorobenzidine, 5.4%	3870	630	2000	59	1490	76
Polyethylene adipate	Toluene, 13%	Tolylenediamine, 3%	4070	720	2090	51	500	60
Polyethylene adipate	Toluene, 13%	Dianisidine, 6.5%	3970	635	2630	37	460	58
Polyethylene adipate	Toluene, 13%	Diaminophenetol, 3.3%	3030	602	1670	45	460	65
Polyethylene adipate	Hexamethylene, 13%	4,4'-Diaminodiphenylmethane, 5%	3900	680	3010	53	1170	90
Polyethylene adipate	Hexamethylene, 13%	Dianisidine, 6.5%	3150	650	1490	55	730	77
Polyethylene adipate	Hexamethylene, 13%	Tolylenediamine, 3%	3840	710	2090	57	570	69
Polypropylene adipate	Hexamethylene, 13%	Tolylenediamine, 3%	1830	707	1600	54	370	70
70/30 Mixture*	Hexamethylene, 13%	Tolylenediamine, 3%	3080	728	1370	51	360	65
Uncastable combinations								
70/30 Mixture*	1,5-Naphthalene, 16%	Tolylenediamine 2.64%	4650	660	2400	57	1310	72
70/30 Mixture*	1,5-Naphthalene, 16%	1,5 Naphthalenediamine, 3.4%	2860	430	2560	63	1620	69
70/30 Mixture	1,5-Naphthalene, 16%	Diaminodiphenylmethane, 4.2%	3920	590	2790	60	1520	72
70/30 Mixture	1,5-Naphthalene, 16%	Dichlorophenylendiamine, 3.8%	1330	340	533	45	720	72

* See note, Table I.

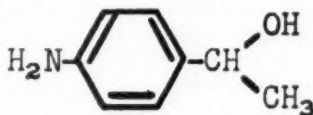
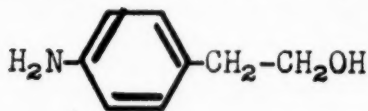
bination of a highly reactive diisocyanate with a less reactive diamine, or vice versa. The ester itself exerts no influence on the reaction rate between the isocyanate ester and the diamine. Since as with glycol cross-linking there is no gas formation, amine cross-linking enables processing in the fluid state. A sure criterion of the reactivity between the diisocyanate and the diamine is given by the reaction velocity of the two components in boiling methylene chloride. If, on mixing half-normal solutions of the two, there is an immediate precipitate as a result of urea formation, processing in the fluid state will be impossible if this combination is used in the polyester system. Only with an interval of at least 25 to 30 seconds before the appearance of turbidity in the methylene chloride solution will processability in the fluid state be assured. For example, by the use of 1,5-naphthalene diisocyanate and dichlorobenzidine, a castable material is obtained which is characterized by its good fluidity, whereas with benzidine instead of dichlorobenzidine, this processing technique is no longer possible. Similarly, by use of hexamethylene diisocyanate and tolylenediamine, a pourable melt is obtained which is easily handled. Likewise, tolylene diisocyanate in combination with *o*-dichlorobenzidine or dianisidine is suitable. With amine cross-linking, one is no longer limited to the reactive so-called "bulky and open" diisocyanates, but can use practically any diisocyanate in combination with appropriate diamines.

Amine cross-linking is carried out as follows. First, the diisocyanate is added in the usual manner to the dried polyester. The excess of isocyanate is again so measured that about 2-3 polyester chains are coupled together. The appropriate diamine is then added to the melt at about 120 to 130°. The weight ratios are so chosen that the diamine content is less than that calculated for isocyanate. After thorough mixing the mixture is poured into the desired form. The final state of cure is reached by heating 4-5 hours at 100° C. Press processing or the combined cast-press technique may also be used.

In addition to reaction velocity, the mechanical properties are also influenced by the diisocyanate-diamine combination. Thus, with hexamethylene diisocyanate products of low modulus are obtained, whereas, 1,5-naphthalene diisocyanate gives products of high modulus. By means of the variety of possible combinations, it is possible to vary the overall properties of the products in any particular desired manner.

Table III gives a summary of castable combinations, as well as certain combinations no longer castable, but which can be worked satisfactorily by the pressing process.

In addition to diamines, aminoalcohols can be used as cross-linking agents. In this way a combination of both procedures is realized. *p*-Aminophenyl ethanol and *p*-aminophenyl methyl carbinol are particularly suitable.



Instead of amino alcohols, mixtures of glycols and diamines can also be used in which case the overall properties of the final product vary in a specific manner for each cross-linking agent.

The amino alcohols are especially important in the preparation of milled sheets which are stable in storage¹⁰. It is known that sheets made for subsequent pressing can be kept for only a limited time. After only a few days of

TABLE IV

Polyester	Diisocyanate	Cross-linking agent	Tensile strength (lb. per sq. in.)	Elongation at break (%)	Tear strength (lb. per sq. in.)	Rebound elasticity (%)	300% Modulus (lb. per sq. in.)	Shore hardness
70/30 Mixture*	1,5 Naphthalene, 16%	<i>p</i> -Aminophenyl-methyl carbinol, 2.95%	4490	650%	1890	53	940	71
70/30 Mixture*	1,5 Naphthalene, 16%	{ <i>o</i> -Dichlorobenzidine, 1.8% 1,4-CyclohexanedioI, 1.66% }	3130	620	1540	47	1080	70

* See note, Table I.

TABLE V

Polyester	Diisocyanate	Cross-linking agent	Diisocyanate added before curing	Tensile strength (lb. per sq. in.)	Elongation (%)	Tear strength (lb. per sq. in.)	Rebound elasticity (%)	300% Modulus	Shore hardness
Polyethylene adipate OH Number 53	1,5-Naphthalene, 16%	Ethanolamine, 1.65%	1,5-Naphthalene, 2%	3610	730%	2060	55	880	65
Polyethylene adipate OH Number 53	1,5-Naphthalene, 16%	Ethanolamine, 1.65%	1,5-Naphthalene, 4%	3780	650	2660	57	1000	66
70/30 Mixture*	1,5-Naphthalene, 17%	Ethanolamine, 2%	1,5-Naphthalene, 3%	4300	710	2180	46	1290	75
Polyethylene adipate OH Number 53	Toluene, 12.4%	Ethanolamine, 1.65%	1,5-Naphthalene, 3%	4550	707	1120	48	1460	53
60/40 Mixture*	1,5-Naphthalene, 14%	Dichlorobenzidine, 3.3%	1,5-Naphthalene, 3%	3500	385	2130	51	2590	70
60/40 Mixture*	1,5-Naphthalene, 14%	1,4-CyclohexanedioI, 3.3%	1,5-Naphthalene, 5%	1830	625	820	46	—	—

* See note, Table I.

TABLE VI

Polyester	Diisocyanate	Cross-linking agent	Tensile strength (lb. per sq. in.)	Elongation at break (%)	Tear strength (lb. per sq. in.)	Shore hardness
Polyethylene adipate OH Number 53	Toluene, 38%	<i>o</i> -Dichlorobenzidine, 39.5%	3790	121	3740	99
Polyethylene adipate OH Number 53	Toluene, 38%	Tolylenediamine, 19.3%	2220	117	1760	95
Polyethylene adipate OH Number 53	Toluene, 38%	2,4'-Diaminobiphenyl, 29%	2530	164	1000	98
Polyethylene adipate OH Number 53	1,5-Naphthalene, 30%	<i>o</i> -Dichlorobenzidine, 21.6%	3600	284	—	96

exposure to the air the material undergoes changes such that it can no longer be pressed satisfactorily by the usual operating conditions. The thermoplasticity decreases sharply and the molded pieces obtained have rough surfaces.

The limited storage life of milled sheets, which complicates fabrication operations considerably, is apparently due to a cross-linking reaction. The condensation product obtained by the various cross-linking processes still contains free isocyanate groups, since an amount of cross-linking agent which was less than equivalent to the isocyanate content was used. These isocyanate groups react during storage, even at room temperature, with atmospheric moisture to form urea groups, which lead to cross-linking in a known manner. The limited storability is eliminated only if care is taken that the condensation product does not contain free isocyanate groups. This is done by treating the chain-lengthened isocyanate ester by an amount of cross-linking agent which is equivalent or more than equivalent to the free isocyanate content. In this manner, all the isocyanate groups are used up, and the condensation products so obtained have unlimited storage life. For this purpose amino alcohols, diamines and glycols, or mixtures of these, are suitable. Prior to molding, there is mixed into the milled sheet a small amount of diisocyanate, which leads to final cross-linking. The mixing is best done on the mill. The diisocyanate then reacts in the press in a known manner with the previously formed urea groups. By this procedure slabs were prepared which were press-cured satisfactorily after six months of storage. They still retained good plasticity. The products obtained therefrom had the physical properties shown in Table V.

INFLUENCE OF THE CHAIN-LENGTHENING REACTION

Whereas up to this point the cross-linking reaction has received primary emphasis, the chain lengthening reaction which leads to the isocyanate ester will now be considered. The excess of isocyanate was previously so measured that a lengthening occurred. Further increase of the amount of diisocyanate would repress the lengthening reaction and increase the content of free isocyanate groups. If an excess of 100 per cent over the amount calculated from the hydroxyl number is used, essentially no chain-lengthening occurs, and the effect consists simply of converting the hydroxylpolyester to an isocyanate polyester. Further increase of the amount of diisocyanate results in the presence of unreacted diisocyanate in the mixture. Subsequent treatment with cross-linking agents such as diamines or glycols effects a coupling of isocyanate polyester through urea or urethane bridges. Free diisocyanates react to form polyureas or polyurethanes. Since, in general, a molecular deficiency of cross-linking agent with respect to free isocyanate groups is used, there are always free isocyanate groups remaining, which react with the urea or urethane groups to establish cross-linking. The finished product may, therefore, be considered as a polyurea, or polyurethane, into which polyester units which function as softeners are built.

Products are thus obtained which have particularly good physical properties and which are also characterized by good resistance to acids and alkalies¹¹. This is the more surprising, since polyureas of themselves, in contrast to polyurethanes, show very poor physical properties. Therefore, we gave special attention to the products containing polyureas.

The character of the materials is primarily determined by the amounts of

the excess of diisocyanate and of cross-linking agent. By use of a 150–200 per cent excess, a considerable decline of elasticity in comparison to that of the normal products occurs. By further increase of diisocyanate and cross-linking agent to 300–400 per cent, the elasticity and elongation decrease, while the hardness increases and very good tensile strengths and tear strengths are obtained. In spite of their hardness, these products are not brittle, as are phenol-formaldehyde or urea-formaldehyde resins. Only by use of an excess of over 500 per cent of diisocyanate does the product become so inelastic that it breaks on bending.

Besides the relative proportions, the structure of the diisocyanates and diamines used play a significant part. Among diisocyanates, tolylene diisocyanate, 1,5-naphthalene diisocyanate and nitrobiphenyl diisocyanate, have proved particularly suitable. In contrast to the processes described previously, triisocyanates such as triphenylmethane triisocyanate can also be used. Processing can be carried out in the fluid as well as the solid state. For fluid-state processing, the diisocyanate-diamine combination is again very significant. That is, a reactive isocyanate must be used only with a relatively unreactive diamine, and vice versa. The procedures for diamine cross-linking are also applicable here. By fluid-state processing it is possible to cast molded goods or films of leatherlike quality. Because of the high dielectric constant of the materials, the casting process is of interest in the electrical industry for the coating of condensers, pouring around cable joints, etc. If solid-state processing is preferred, the condensation is carried out in a mixer, whereby a product is obtained which can be formed under pressure satisfactorily without further milling, even after aging four weeks. In both processes significant amounts of fillers can be worked in. In particular, talc, titanium dioxide, asbestos, mixtures of asbestos, and iron powder have proved satisfactory.

Although in the previously described methods, the polyester was strictly linear, branch-chained polyesters, which in addition to bifunctional components also contain trifunctional units, such as glycerol, trimethylolpropane, etc., can also be used. Also mixtures of esters or esters made from mixed reactants are suitable. Table VI summarizes the physical properties of some of the combinations.

SUMMARY

In the 6th Communication¹² on the general subject of urethanes, it was shown that, in the presence of an excess of a diisocyanate, in particular naphthalene 1,5-diisocyanate, linear polyesters of adipic acid and simple glycols simultaneously lengthen and become converted into so-called polyester isocyanates, with the isocyanate groups as terminal groups of the chains.

While this earlier work was concerned with the problem of cross-linking to form the synthetic elastomer, Vulcollan, with water as the agent, the work described in the present paper deals with other cross-linking agents, including glycols, aminoalcohols, diamines, and other bifunctional compounds.

The mechanism of cross-linking is discussed for each of these cases, and it is shown that the chemical nature of the cross-linking agent has a decisive influence on the properties of the resulting Vulcollan product.

The methods of preparation which are described point the way to new manufacturing processes, particularly the possibility of molding Vulcollan without having to use a solvent.

REFERENCES

- ¹ German patent application F 2907 39/C (July 10, 1944); Bayer, Müller, Petersen, Piepenbrink, and Windemuth, *Angewandte Chem.* **62**, 57 (1950); *RUBBER CHEM. & TECHNOL.* **23**, 812 (1950).
- ² Ladenburg, *Ber.* **2**, 30 (1869).
- ³ Work of H. Rinke.
- ⁴ German patent application F 2824 39/C (Jan. 17, 1944); F 2972 39/C (Apr. 12, 1944).
- ⁵ Nageli and Tyabji, *Helv. Chim. Acta* **17**, 947 (1934).
- ⁶ This formula, actually an amide, was apparently intended to be a urea.
- Reference 5 cites many cases where the reaction of an aryl isocyanate with a carboxylic acid gives significant yields of the symmetrical diarylurea and the anhydride of the carboxylic acid. The following mechanism is proposed:

$$\begin{aligned} & \text{R-NCO} + \text{R'COOH} \longrightarrow \text{R-NH-CO-O-CO-R'} \\ & 2 \text{R-NH-CO-O-CO-R'} \longrightarrow \text{R-NH-CO-O-CO-NH-R} + \text{R'CO-O-CO-R'} \\ & \text{R-NH-CO-O-CO-NH-R} \longrightarrow \text{R-NH-CO-NH-R} + \text{CO}_2 \quad [\text{Translator}] \end{aligned}$$
- ⁷ Müller, Piepenbrink, Schmidt, and Weinbrenner, German patent 831,722 (Feb. 24, 1949) (U. S. Priority, Jan. 12, 1949).
- ⁸ This should probably be hexahydrocatechol (1,2-cyclohexanediol); see Table 1.
- ⁹ Müller, German patent 836,826 (Feb. 24, 1949).
- ¹⁰ Schmidt and Müller, German patent 838,652 (Feb. 24, 1949).
- ¹¹ Müller and Petersen, German patent 831,604 (Feb. 24, 1949).
- ¹² Bayer, Müller, Petersen, Piepenbrink, and Windemuth, *Angew. Chem.* **62**, 57 (1950); *RUBBER CHEM. & TECHNOL.* **23**, 812 (1950).

VARIABLES CONTROLLING THE CROSS-LINKING REACTIONS IN RUBBER*

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There is general acceptance of the theory that vulcanization of rubber with sulfur results from a chemical reaction in which intermolecular sulfur cross-links are formed. Supplementary chemicals such as accelerators, metal oxides, and fatty acids are employed to make the reaction faster and to increase the yield of cross-links.

That sulfur may react with rubber and compounding ingredients in various ways to give diversified reaction products is well known. Reactions of sulfur which lead to products other than intermolecular cross-links do not enhance vulcanization, and may be considered side reactions of secondary importance. Insufficient knowledge of the manner in which temperature of cure and concentration of compounding ingredients affect the yield of cross-links in the vulcanization reaction has led to the general belief that little or no dependence exists between physical properties and combined sulfur.

In the present paper the relationship between the vulcanization variables and yield of cross-links is described. It is shown that when these variables are controlled in such a way as to give the greatest yield of cross-links, a definite reproducible relationship exists between physical cure (stress at 200 per cent elongation) and combined sulfur.

DETERMINATION OF YIELD OF CROSS-LINKS IN VULCANIZATION REACTION

In general, the more highly vulcanized the rubber compound, the higher is its modulus. It is, therefore, natural to suppose that modulus, or retractive force, is directly related to the number of cross-links. Wall¹ and Flory² have reduced these generalities to precise mathematical terms. Based on the entropy change which occurs when a vulcanized polymer is stretched, an equation has been derived which shows that the equilibrium retractive force—in other words, stress at a given elongation—is a linear function of the number of cross-links per unit volume. For pure-gum compounds a constant relationship has been found to exist between equilibrium retractive force at 200 per cent elongation and the retractive force at 200 per cent elongation, determined in the first elongation cycle. Since all the compounds employed in the investigations described at this time are pure-gum compounds, the nonequilibrium stress at 200 per cent elongation obtained on the first elongation cycle is used as a measure of the relative number of cross-links present.

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TABLE I
EFFECT OF TIME AND TEMPERATURE OF VULCANIZATION ON STRESS

Time of cure (hours)	Stress at 200% elongation (lb. per sq. in.)							
	70° C	80° C	90° C	100° C	110° C	120° C	140° C	160° C
0.25								155
0.50							165	180
0.75							195	180
1							200	180
2				65	110	165	210	
4				95	160	200		
8				135	210	250		
16			150	190	265	260		
24			180	240	280			
32			215	260				
48			250	290				
64			285	300				
80			310	300				
168			325					
252		265	320					
336		265						
432	210							
528	210							

EFFECT OF VULCANIZATION VARIABLES ON YIELD OF CROSS LINKS

Effect of Time and Temperature of Vulcanization.—In a study of the effect of vulcanization reactants on the yield of sulfur cross-linked products, it is desirable to select time and temperature of reaction which are most favorable for a high yield of cross-links.

The effect of the temperature of cure on the relative yield of cross-links was determined in a compound containing one part of sulfur and quantities of zinc

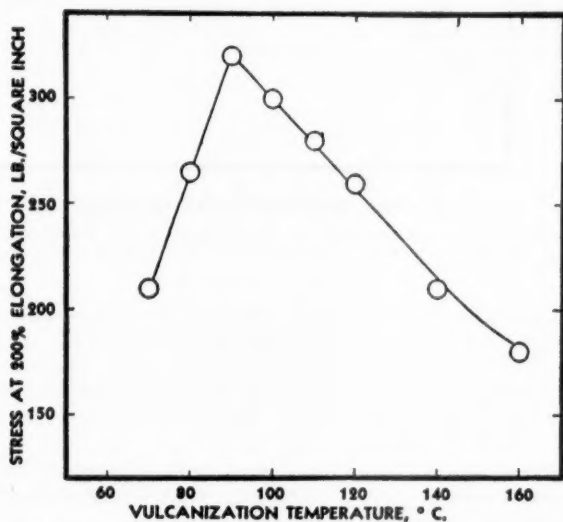


FIG. 1.—Effect of vulcanization temperature on cross-linking reaction. Compounds contain sulfur 1.0, zinc oxide 10.0, lauric acid 10.0, and MBT 2.0 parts per 100 grams of rubber. Refer to Table I for times of cure.

oxide, lauric acid, and 2-mercaptobenzothiazole in excess of the amounts necessary for the greatest yield of cross-links. The choice of composition is made clear in the following sections.

Times of cure were varied at each temperature, as shown in Table I, to make sure that the vulcanization reaction was carried to completion.

The maximum stress obtained at each curing temperature is shown in Figure 1. This figure shows that the yield of cross-links increases with decreasing temperature of cure until 90°C is reached. Curing temperatures lower than 90°C result in lower yields of cross links.

Nearly maximum cross-linking is obtained at 100°C and, since it is more convenient to cure at this temperature than at 90°C, this temperature was used for the greater part of these investigations.

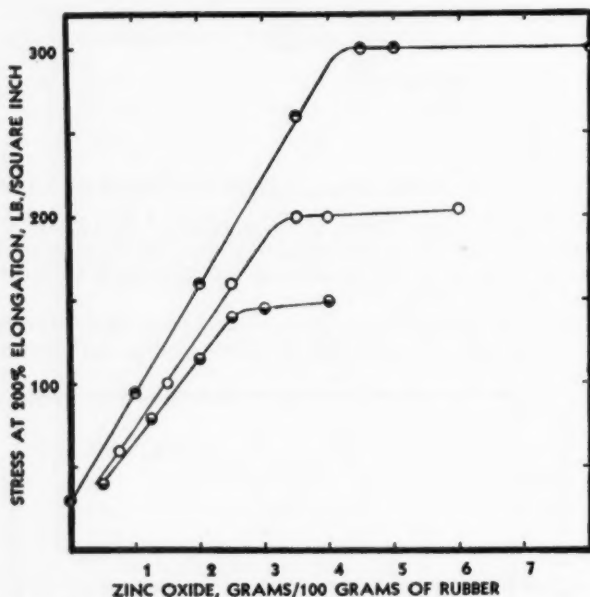


Fig. 2.—Effect of zinc oxide concentration on cross-linking reaction. Compounds contain sulfur 0.40 ●, 0.65 ○, or 1.00 ●, lauric acid 10.0, MBT 3.0, and variable amounts of zinc oxide per 100 grams of rubber. Cured 64 hours at 100° C.

Effect of Zinc Oxide, Lauric Acid, and 2-Mercaptobenzothiazole Concentrations.—Farmer³, in a review on vulcanization, states that "the role of the oxide (zinc oxide) in the vulcanization process has never been determined, although much discussion has taken place on the subject". However, it is recognized in rubber technology that, for best results, thiazole accelerators require the presence of both zinc oxide and fatty acid.

In the present investigation, the effect of each of the variables, zinc oxide, lauric acid, and 2-mercaptobenzothiazole on the yield of cross-links in the vulcanization reaction was studied separately.

The main features of the effect of zinc oxide in the presence of a rubber compound containing 2 parts of mercaptobenzothiazole and 10 parts of lauric

acid per 100 grams of rubber is given in Figure 2. Each point on this curve represents the maximum stress at 200 per cent elongation obtained when this compound, containing the indicated amount of zinc oxide, is vulcanized at 100°C.

For a given amount of sulfur, an almost linear increase in stress at 200 per cent elongation occurs as the zinc oxide is increased to a point, after which additional zinc oxide has no appreciable effect. The quantity of zinc oxide required for the maximum yield of cross-links is a function of the amount of sulfur present.

The effect of lauric acid concentration was studied in a formula containing 2 parts of 2-mercaptobenzothiazole and 10 parts of zinc oxide per 100 grams of rubber. The vulcanization procedure used was the same as that employed in the zinc oxide studies.

The main characteristics of the relationship between lauric acid and the cross-linking reaction, shown in Figure 3, are similar to those obtained with

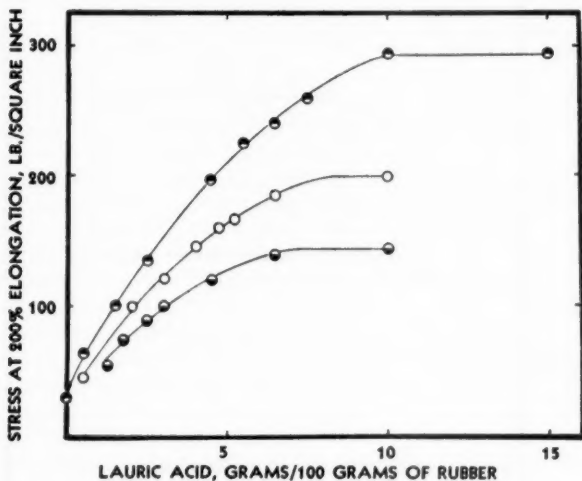


Fig. 3.—Effect of lauric acid concentration on cross-linking reaction. Compounds contain sulfur 0.40 ●, 0.65 ○, or 1.00 ●, zinc oxide 10.0, MBT 3.0, and variable amounts of lauric acid per 100 grams of rubber. Cured 64 hours at 100°C.

zinc oxide. A nearly linear increase in stress at 200 per cent elongation is obtained as lauric acid is increased at constant initial sulfur concentration, until the greatest yield of cross-links is obtained. Beyond the critical point defined by the intersection of the straight lines, giving the initial effect of lauric acid, and the final maximum amounts, very little additional cross-linking occurs.

The effect of 2-mercaptobenzothiazole concentration on the development of cross-links in a compound containing 10 parts of zinc oxide and 10 parts of lauric acid per 100 grams of rubber is shown in Figure 4. The rate of sulfur combination as affected by variation in accelerator content is not considered. In all cases, irrespective of rate of cure, the vulcanization reaction was carried to completion. Cures were carried out at 110° instead of at 100°C, in order to get a faster rate of sulfur combination, since relatively small amounts of 2-mercaptobenzothiazole were used in some of the compounds.

It will be noted in this work that the relative number of cross-links increases with increasing 2-mercaptobenzothiazole concentration up to a point. Beyond this point further additions of accelerator result in no further increase.

The amount of 2-mercaptobenzothiazole required for a maximum yield of cross-links appears to be relatively independent of the amount of sulfur present. This is in contrast to the effect of sulfur content on the amount of zinc oxide and lauric acid required for maximum physical cure.

The results shown in Figures 2, 3, and 4 clearly demonstrate that if any one of the three necessary vulcanization ingredients is not included in the rubber

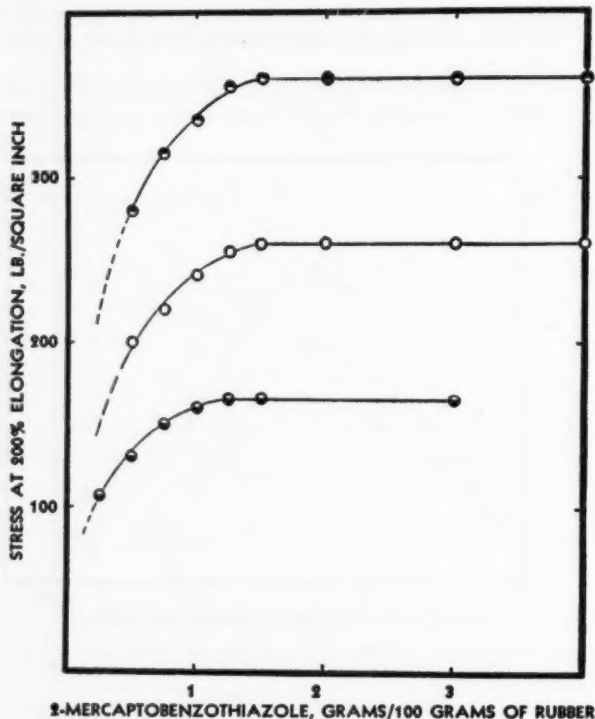


Fig. 4.—Effect of accelerator concentration on cross-linking reaction. Compounds contain sulfur 0.50 ●, 1.00 ○, or 1.50 ◐, zinc oxide 10.0, lauric acid 10.0, and variable amounts of MBT per 100 grams of rubber. Cured 64 hours at 110° C.

formula, only a negligible number of cross-links is formed. It is possible that the effective promoter of the cross-linking reaction is a rubber-soluble reaction product of 2-mercaptobenzothiazole, zinc oxide, and lauric acid. The following reactions which occur in benzene indicate that complex zinc compounds are formed in rubber: (1) zinc oxide plus lauric acid forms zinc laurate, (2) zinc oxide plus 2-mercaptobenzothiazole forms a mixture of the neutral and the basic zinc salt, (3) zinc laurate plus 2-mercaptobenzothiazole forms a benzene-soluble complex containing up to 2 moles of the thiazole per mole of zinc laurate, and (4) zinc laurate plus the mixture of neutral and basic zinc salts of 2-mercap-

TABLE II

TABLE II. EFFECT OF TIME AND TEMPERATURE OF VULCANIZATION ON YIELD OF SULFIDE SULFUR

Time of cure (hours)	Sulfide sulfur (grams per 100 grams of rubber)						
	70° C	80° C	90° C	100° C	110° C	120° C	140° C 160° C
0.25							0.29
0.50							0.25 0.36
0.75							0.31 0.38
1							0.37 0.43
2				0.04	0.10	0.17	0.42
4				0.08	0.21	0.26	
8				0.14	0.26	0.36	
16			0.14	0.22	0.37	0.42	
24			0.18	0.30	0.41		
32			0.21	0.32			
48			0.26	0.37			
64			0.31	0.40			
80			0.32	0.42			
168			0.37				
252		0.34	0.39				
336		0.36					
432	0.27						
528	0.28						

tobenzothiazole forms a benzene-soluble complex containing up to 2 moles of the zinc salt of the thiazole per mole of zinc laurate.

The concentration of these complex zinc compounds in rubber depends on the relative amounts of 2-mercaptobenzothiazole, zinc oxide, and lauric acid. If the concentration of any one of these variables is reduced to zero, it follows that the concentration of the soluble complex is also zero. In this case, as is shown in Figures 2, 3, and 4, little vulcanization occurs in compounds containing relatively small amounts of sulfur.

The requirements of zinc oxide and fatty acid described at this time have been determined for compounds accelerated with 2-mercaptobenzothiazole and are not necessarily the same for other accelerators. The zinc oxide and fatty acid requirements of various types of accelerators will be described in a later publication.

Effect of Sulfur Concentration.—In vulcanization studies reported in the literature, little or no relationship has been shown to exist between physical properties and combined sulfur except in the case of a given mixture, and then only when the vulcanization reaction is not carried to completion. This lack of dependence of physical cure on combined sulfur has been frequently used as an argument against the sulfur-cross linking theory of vulcanization.

TABLE III. EFFECT OF SULFUR CONCENTRATION ON STRESS AND SULFIDE SULFUR

Rubber	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10
Lauric acid	10	10	10	10	10	10
2-Mercaptobenzothiazole	2	2	2	2	2	2
Sulfur	0.125	0.25	0.50	0.75	1.0	1.25

(All compounds were vulcanized 64 hours at 100° C)

Stress at 200% elongation	70	110	170	235	300	360
Sulfide sulfur	0.05	0.10	0.19	0.30	0.39	0.49
Sulfide sulfur/total sulfur	0.40	0.40	0.38	0.40	0.39	0.39

In light of the marked dependence of the cross-linking reaction on the variables: time, temperature, and concentration of zinc oxide, fatty acid, and accelerator, which has been demonstrated in preceding sections, it is not surprising that little or no relationship has been found.

The effect of sulfur concentration on the physical cure of compounds containing sufficient zinc oxide, lauric acid, and 2-mercaptobenzothiazole to ensure the greatest yield of cross-links is shown in Table III and Figure 5. Even when the amount of sulfur is varied ten-fold, the stress at 200 per cent elongation is a linear function of the sulfur.

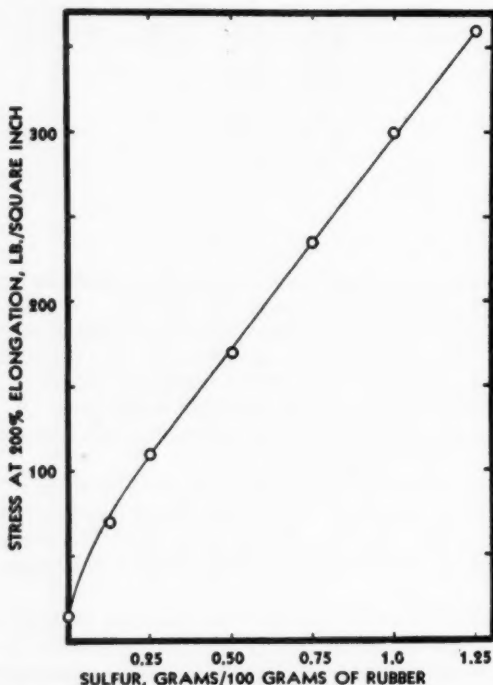


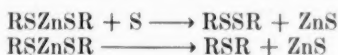
Fig. 5.—Effect of sulfur concentration on extent of vulcanization. Compounds contain zinc oxide 10.0, lauric acid 10.0, MBT 2.0, and variable amounts of sulfur per 100 grams of rubber. Cured 64 hours at 100° C.

It is apparent from these results that under controlled conditions a linear relationship exists between retractive force and the amount of sulfur added to the compound.

RELATION BETWEEN SULFIDE SULFUR AND NUMBER OF CROSS-LINKS

Armstrong, Little, and Doak⁴ report that, in the presence of vulcanizing ingredients, zinc sulfide and allyl type sulfides and disulfides are produced in the reaction of sulfur with certain olefins. They also point out that in accelerated rubber compounds containing zinc oxide and fatty acid, the inorganic

sulfide sulfur formed during vulcanization is much more closely related to the degree of cross-linking than is the combined sulfur. On the basis of these results they propose that, in the vulcanization reaction, zinc mercaptides are formed, which react with free sulfur to produce disulfides plus zinc sulfide or spontaneously decompose to form monosulfides plus zinc sulfide.



Either of these mechanisms leads to the conclusion that sulfide sulfur should be a measure of the number of cross-links formed during vulcanization.

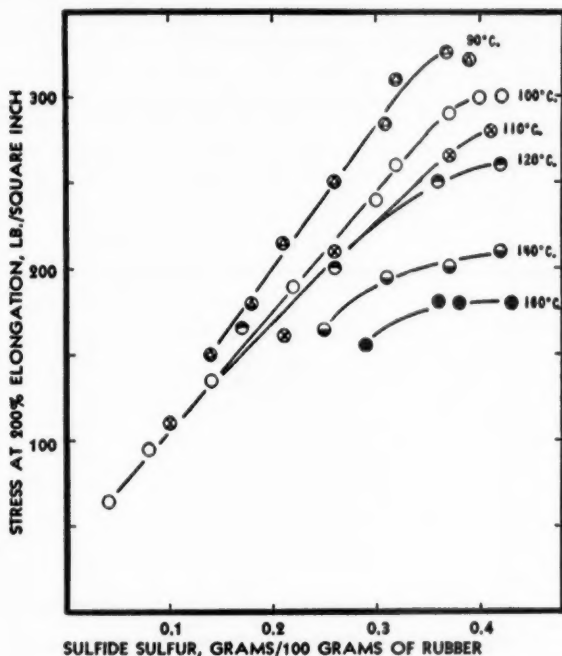


FIG. 6.—Effect of vulcanization temperature on relationship between retractive force and sulfide sulfur. Compounds contain sulfur 1.0, zinc oxide 10.0, lauric acid 10.0, and MBT 2.0 parts per 100 grams of rubber. Refer to Table II for times of cure.

Hull, Olsen, and France⁵ investigated the formation of inorganic sulfide produced in rubber and copolymers of isoprene-styrene and butadiene-styrene. They agreed that in some vulcanizates, such as those described by Armstrong, Little, and Doak, there appears to be justification for associating the modulus-building reaction with that which forms zinc sulfide. However, they showed that in some compounds there was little or no indication that sulfide sulfur correlated with the cross-linking reaction.

Experimental results presented below show the effect of time and temperature of cure and the concentration of vulcanization ingredients on the relationship between number of cross-links (retractive force) and sulfide sulfur.

Effect of Temperature of Vulcanization.—The effect of temperature of vulcanization on the relationship between sulfide sulfur and stress at 200 per cent elongation is shown in Figure 6. These data are taken from Tables I and II.

A linear relationship is found between retractive force and sulfide sulfur throughout most of the course of the vulcanization reaction when vulcanization is carried out at temperatures of 90° to 110°C. At temperatures above 110° C, marked deviations from linearity occur, particularly at the higher temperatures and toward the end of the vulcanization reaction.

Insufficient data are available at this time to indicate the relationship between sulfide sulfur and retractive force for compounds vulcanized at temperatures below 90°C. The few points given in Table I indicate that, at curing temperatures below 90°C, a larger amount of zinc sulfide is formed for a given number of cross-links than is formed at 90°C.

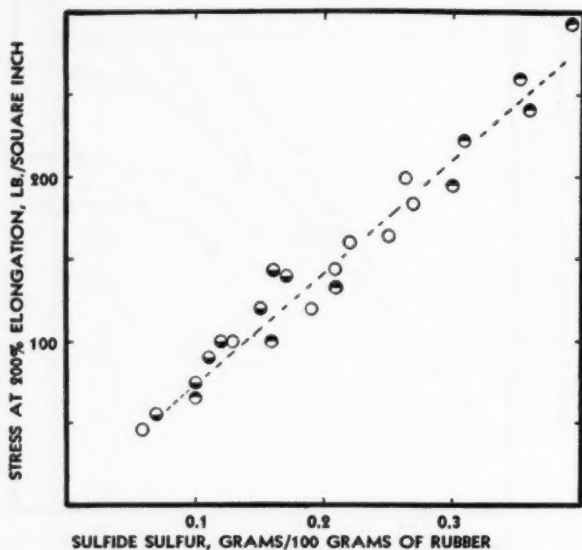


Fig. 7.—Effect of lauric acid concentration on relationship between retractive force and sulfide sulfur. Compounds contain sulfur 0.40 ●, 0.65 ○, or 1.00 ◐, zinc oxide 10.0, MBT 3.0, and variable amounts of lauric acid per 100 grams of rubber. Cured 64 hours at 100° C.

The linear relationship which exists between retractive force and sulfide sulfur under the temperature conditions which lead to the maximum yield of cross-links suggests that, under these conditions, the formation of sulfide sulfur is closely associated with formation of cross-links. Under optimum conditions this relationship may even be stoichiometric. However, because the retractive force for a given amount of sulfide sulfur increases with decreasing temperature of vulcanization from 110° to 90°C, it is difficult to determine whether a one to one relationship is approached at 90°C or whether a one to one relationship is obtained at a higher temperature, *e.g.*, 110°C. In the latter case more than one cross-link would be formed per atom of sulfide sulfur at the lower temperatures

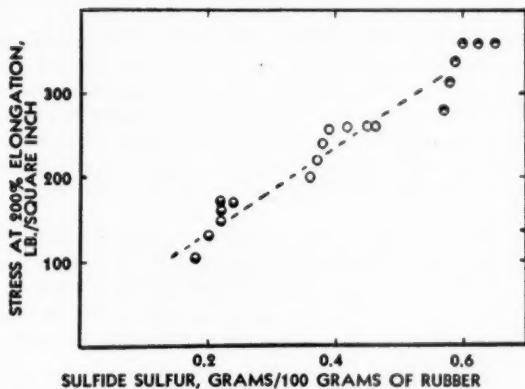


FIG. 8.—Effect of accelerator content on relationship between retractive force and sulfide sulfur. Compounds contain sulfur 0.50 ●, 1.00 ○, or 1.50 ●, zinc oxide 10.0, lauric acid 10.0, and variable amounts of MBT per 100 grams of rubber. Cured 64 hours at 110° C.

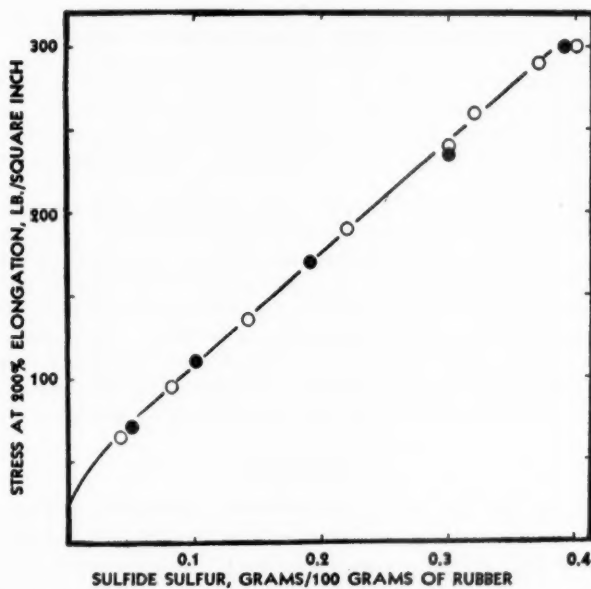


FIG. 9.—Effect of sulfur concentration on relationship between retractive force and sulfide sulfur. ● Compounds contain variable amounts of sulfur, zinc oxide 10.0, lauric acid 10.0, and MBT 2.0 parts per 100 grams of rubber and were cured 64 hours at 100° C. Refer to Table III. ○ Compounds contain sulfur, 1.0, zinc oxide 10.0, lauric acid 10.0, and MBT 2.0 parts per 100 grams of rubber and were cured variable times at 100° C. Refer to Table I.

of vulcanization. This problem will be considered in greater detail in a later publication.

Effect of Lauric Acid, Zinc Oxide, and 2-Mercaptobenzothiazole Concentration.—In Figure 3 the yield of cross-links during vulcanization is shown to be a function of the lauric acid concentration. The relationship between sulfide sulfur and retractive force for these compounds is shown in Figure 7.

Even though variation in fatty acid concentration gives wide variations in the stress at 200 per cent elongation, sulfide sulfur appears to be in all cases closely associated with the formation of cross-links. All the compounds were cured 64 hours at 100°C.

The relationship between sulfide sulfur and retractive force in stocks containing a given amount of lauric acid and variable zinc oxide concentration is confused because of the softening action of free fatty acid. As a result, the effect of zinc oxide concentration on sulfide sulfur formation will not be discussed.

The effect of accelerator content on the relationship between sulfide sulfur and retractive force is shown in Figure 8.

These data indicate that although there is a measure of correlation between sulfide sulfur and retractive force, it is not close. This conclusion is in general agreement with that of Hull, Olsen, and France⁵, who found that, although retractive force increased with increasing concentration of accelerator, no change occurred in the formation of sulfide sulfur.

Effect of Sulfur Concentration.—In Figure 6, it is shown that, when sufficient zinc oxide, lauric acid, and 2-mercaptobenzothiazole are present to give a maximum yield of cross-links, a linear relationship exists between stress at 200 per cent elongation and the sulfur added to the compound.

The variable stress at 200 per cent elongation recorded in Table III is a result of variable sulfur content. Time of vulcanization is the same for all. Variable retractive force has also been obtained for a compound of given sulfur content by variation in time of vulcanization. These data are recorded in Tables I and II.

The relationship between sulfide sulfur and retractive force for the two series of compounds cured at 100°C, is shown in Figure 9.

It is apparent that when sufficient quantities of vulcanization reactants are present and when vulcanization is carried out at a temperature as low as 100°C, the linear relationship between sulfide sulfur and retractive force is independent of either time of cure or initial concentration of sulfur. No conclusion can be drawn at this time as to whether a molecule of zinc sulfide is formed for each cross-link formed during vulcanization, but there is strong circumstantial evidence that this may be nearly the case when a maximum yield of cross-links is obtained.

SUMMARY

During vulcanization, sulfur reacts with rubber and compounding ingredients in various ways to give diversified reaction products. Only the sulfur that forms cross-links between rubber molecules contributes to the transformation of rubber from the plastic to the elastic state. Reactions of sulfur which lead to products other than intermolecular cross-links are considered side reactions of secondary importance to vulcanization.

This study was initiated to determine in a relatively quantitative manner the effect of time, temperature, and concentration of reactants on the yield of intermolecular cross-links in the 2-mercaptobenzothiazole-accelerated sulfur-

vulcanization of Hevea rubber. This investigation was considered a necessary step in a study of the over-all mechanism of the vulcanization reactions.

When conditions necessary for the greatest yield of cross-links per unit of combined sulfur are followed, a linear relationship exists between stress at 200 per cent elongation (a measure of the relative number of cross-links) and combined sulfur. Under conditions that lead to a maximum yield of cross-links, a linear relationship exists between retractive force and zinc sulfide.

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- ³ Farmer, in "Advances in Colloid Science", Interscience Publishers, Inc., New York, **1946**, Vol. 2, p. 355.
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STRUCTURE OF ALKALI METAL-CATALYZED BUTADIENE POLYMERS*

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INTRODUCTION

Considerable information has been obtained concerning the structure of butadiene polymers prepared by the free radical mechanism. The effects of variables such as polymerization temperature and ingredients of the polymerization recipe on the polymer structure were determined.¹ It was found that the polymerization temperature governed the resulting structure. Thus with decreasing temperature of polymerization there was an increase in the proportion of *trans*-1,4-butadiene configuration, with an accompanying decrease in *cis*-1,4 and little change in 1,2. It has been widely shown that the reduction in polymerization temperature has the effect of increasing tensile strength, abrasion resistance, and other properties of the polymer.² However, the changes in structure obtained by altering the variables of the emulsion polymerization were relatively limited. In order to complete the knowledge regarding obtainable polybutadiene structures, it appeared to be of interest to determine variations in structure produced by polymerizations having a carbanion type of mechanism such as that obtained with alkali-metal catalysts.

Previous work has shown³ that sodium-catalyzed polybutadiene polymers contained about 70 per cent 1,2-configuration compared to about 20 per cent for emulsion polybutadiene. These sodium polymers were found to have advantages in processing quality and in balance between flex crack growth and hysteresis properties.⁴

The Government Laboratories at the University of Akron prepared alkali metal-catalyzed polybutadiene and butadiene-styrene copolymers in order to investigate the effects of type of catalyst, polymerization temperature, diluents and rate-retarding modifiers upon the structure and the physical properties of the polymers⁵.

EXPERIMENTAL PROCEDURE AND RESULTS

Several series of polybutadienes were made at the Government Laboratories in 8-oz. bottles at 5, 30 and 45°. Three types of catalyst, sodium, potassium and equimolar mixtures of sodium and potassium were used in the following basic formula:

Monomers	100
Diluent	0-300
Rate modifier	0-1.0
Catalyst	0.16-0.30

Illustrative data for the sodium-catalyzed polymers are shown in Table I.

* Reprinted from the *Journal of the American Chemical Society*, Vol. 74, No. 9, pages 2294-2296, May 5, 1952. This paper was presented at the Symposium on Synthetic Rubber at the semiannual meeting of the Division of Rubber Chemistry of the American Chemical Society, New York, September 3-7, 1951.

TABLE I
STRUCTURES OF SODIUM-CATALYZED POLYBUTADIENES

Polymer no.	Polymerization temp. (°C)	Diluent	Structures by infrared		
			1,2 %	trans-1,4 %	cis-1,4 %
1	5	None	74.0	20.0	6.0
2	5	100 pentane	79.5	12.8	7.6
3	5	75 pentane, 25 MCH ^a	77.2	15.3	7.5
30	5	75 pentane, 25 xylene	72.5	21.6	5.9
10	30	None	67.6	24.1	8.3
11	30	100 pentane	66.7	22.1	11.2
12	30	75 pentane, 25 MCH	64.4	23.0	12.6
31	30	75 pentane, 25 benzene	72.9	16.7	10.4
32	30	75 pentane, 25 xylene	61.0	24.5	14.5
21	45	None	60.9	26.4	12.7
23	45	75 pentane, 25 MCH	59.3	24.8	15.9

Because of the more violent reactions with potassium and the mixture of sodium and potassium catalyst, smaller amounts of catalyst and greater amounts of diluents were employed. The diluents were pentane, methylcyclohexane, benzene, and xylene. The rate-modifier employed for all runs to reduce the polymerization rate was 1.0 part dioxane. Unreacted butadiene monomer was vented from the bottles when no visual increase in viscosity was noted, and methanol was added to destroy any unreacted alkali metal.

Sodium-catalyzed polybutadiene and butadiene-styrene copolymers were prepared by the Government Laboratories in a 5-gallon reactor at 30, 40, 60 and 75° according to the above charge formula. The diluents were *n*-butane, methylcyclohexane, pentane, toluene, and xylene. Rate modifiers were dioxane, dodecylamine, piperidine, polyethylene glycol di-(2-ethylhexoate), isopropyl ether and anisyl disulfide. Data for typical polymers are shown in Table II. The raw polymers were processed at the Government Laboratories by soaking in methanol; then 1.5 per cent phenyl- β -naphthylamine and 2 per cent stearic acid (based on wet polymer weight) were added to the batch on a wash mill or in a pelletizer, followed by drying at 60°.

Samples of the polymers were purified at the United States Rubber Company laboratories according to the following method: Approximately 2 grams of polymer was dissolved in 100 cc. of carbon disulfide in a 250-cc. flask and shaken overnight. The solution was filtered through a 300-mesh silk screen to remove gel. The filtered solution was poured slowly into 50 cc. of methanol

TABLE II
STRUCTURES OF SODIUM-CATALYZED POLYBUTADIENES

Diluents: *n*-butane and methylcyclohexane; rate modifier: dioxane; polymerization in 5-gallon reactors

Polymer no.	Polymerization temp. (°C)	Structures by infrared (%)			Second order transition temp., T _s , °C.
		1,2	trans-1,4	cis-1,4	
41	30	73.0	17.6	9.4	-45.5
42	40	72.9	17.3	9.8	-48.5
43	50	68.6	17.6	13.8	-54.0
44	60	66.5	18.6	14.8	-55.0
45	75	69.6	17.1	13.2	-63.5

to precipitate the polymer. The liquor was decanted at intervals and replaced with additional methanol. Nearly all of the carbon disulfide was removed at reduced pressure. Then 5 cc. of 0.04 per cent carbon disulfide solution of antioxidant and 2 cc. of 0.1 per cent carbon disulfide solution of *p*-*t*-butylcatechol were added. The polymer was evacuated to dryness at room temperature. About 50 cc. of carbon disulfide was added to give a 4 per cent solution of the polymer. The solution was filtered through a 300-mesh silk screen before making infrared absorption measurements. The concentration of the polymer solution was determined by withdrawing 5 cc. with a calibrated syringe and placing it in a weighed tin. The weight of dry polymer was determined after drying *in vacuo* overnight.

The techniques used in the infrared absorption measurements to determine the amounts of 1,2-, *trans*-1,4- and *cis*-1,4-configurations have been described by Hart and Meyer⁶ and Hampton⁷. The method of Hampton which was used for these polymers employs polybutadiene standards.

TABLE III
SUMMARY OF POLYBUTADIENE STRUCTURES^a

Catalyst	Polymerization temp. (°C)	1,2 (%)	<i>trans</i> -1,4 (%)	<i>cis</i> -1,4 (%)
Sodium	5	76.0	17.3	6.7
Sodium	30	66.5	22.1	11.4
Sodium	45	60.1	25.6	14.3
Potassium	5	54.0	35.6	10.4
Potassium	30	47.6	37.5	14.9
Potassium	45	46.0	37.5	16.5
K-Na	5	55.5	34.4	10.1
K-Na	30	51.4	35.0	13.6
K-Na	45	49.0	37.0	14.1

^a Average values of bottle runs based on 100 per cent theoretical unsaturation.

Polybutadiene exhibits infrared absorption bands at 724, 911 and 967 cm^{-1} , the relative intensities of which vary, depending on the method of polymer preparation. These bands are due, respectively, to *cis*-1,4-polybutadiene, 1,2-polybutadiene and *trans*-1,4-polybutadiene. From measurement of the absorption at the three positions, the isomeric composition of a sample of polybutadiene is calculated by the solution of three simultaneous equations. This method involves the tacit assumption that no other components are present and that the samples had the theoretical total unsaturation, *i.e.*, one double bond per butadiene unit. The measurements for *trans*-1,4-, *cis*-1,4- and 1,2-configurations sometimes yield a total greater than 100 per cent. This may be due to the fact that the total unsaturation of the polymer standards which were used for calibrating the infrared methods was somewhat lower than the values of the present series of polybutadienes. Extremely accurate unsaturation values by chemical methods are required and work of this type is in progress. For the present comparison it is believed that the relative values of the various types of structure are accurately indicated and that the absolute values may be slightly lower than those reported.

The average values of infrared measurements are shown in Table III for polybutadienes catalyzed by sodium, potassium and equimolar mixtures of these two materials at 5, 30 and 45°. At each temperature it was found that polybutadienes catalyzed by potassium had about 15 per cent lower 1,2-con-

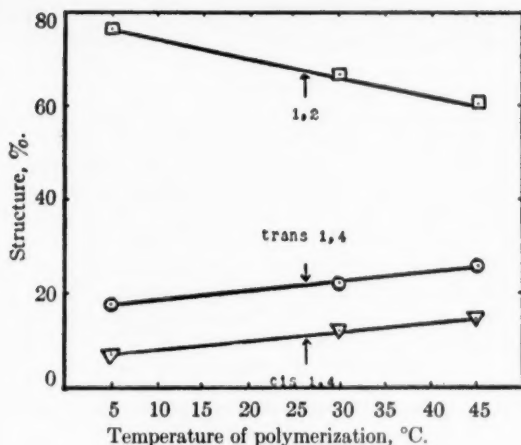


FIG. 1.—Structures of sodium-catalyzed polybutadienes.

figuration than those in which sodium was the catalyst. When mixtures of sodium and potassium were used the results were nearly the same as with potassium catalyst alone.

As the polymerization temperature for sodium-catalyzed polybutadiene decreased, the proportion of 1,2-configuration increased; at the same time the proportion of *cis*-1,4 and *trans*-1,4 decreased. Polybutadienes made at 5° had 10–15 per cent more 1,2-configuration than the 45° polymers, while the 30° polymers were intermediate. The effects of temperature on structure of polybutadienes catalyzed by potassium and by mixtures of potassium and sodium were similar to those described for the sodium-catalyzed polymers. The type of diluent used had little or no effect on the structure of the polybutadienes (Table I).

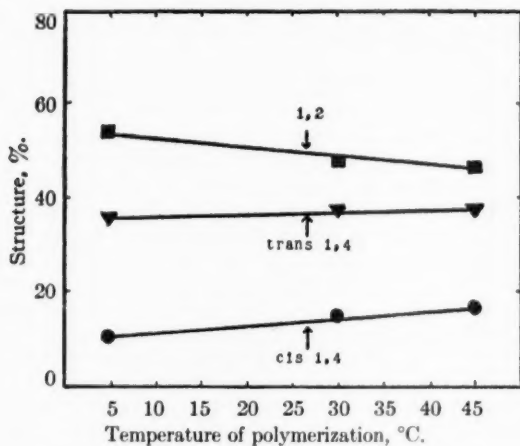


FIG. 2.—Structures of potassium-catalyzed polybutadienes.

The changes in *cis*-1,4-, *trans*-1,4- and 1,2-configuration with polymerization temperature are shown in Figure 1 to be linear for sodium-catalyzed polybutadienes.

Figure 2 shows that the changes in isomeric structure with polymerization temperature for the potassium-catalyzed polybutadienes are also linear.

The infrared data for structure of polybutadienes made in 5-gallon reactors are given in Table II. The effects of polymerization temperature on structure are similar to those described above for the sodium polymers made in 8-oz. bottles. However, results show that polybutadienes prepared in 5-gallon reactors do not have identical structure with polybutadienes made in 8-oz. bottles at the same temperature. It appears that temperatures of polymerization were not as satisfactorily controlled in the 5-gallon reactors.

An important property of a polymeric material is the second-order transition temperature, T_s . A second-order phase transition is manifested as a change in slope when any of the primary thermodynamic properties of a material, such

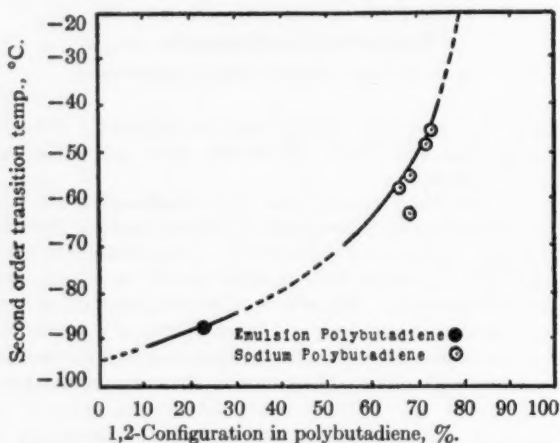


FIG. 3.—Effect of 1,2-configuration on the second-order transition temperature of polybutadiene.

as volume or heat content, are plotted against temperature; and hence as a discontinuity in the first derivative of these properties. Rubber on being cooled below the transition temperature changes from its normal state of toughness and long-range elasticity to a brittle material with little extensibility.

The values of second-order transition temperature here reported were obtained by plotting volume of the rubbers at various temperatures and noting the temperature at which a change in slope occurs. The second-order transition temperatures, T_s , of the polymers are reported in Table II. Thus, the T_s of the sodium-catalyzed polybutadiene made at 30° was -45° whereas the 75° polybutadiene had a T_s of -64°. In Figure 3 we have plotted the second-order transition temperature *vs.* percentage 1,2-structure. The values for free radical-catalyzed polybutadiene previously reported³ are also included in Fig. 3. Since all points fall on a smooth curve, a direct relationship between percentage 1,2-structure and T_s is indicated.

A series of butadiene-styrene copolymers made at 30° at the Government Laboratories were found to have the butadiene with about the same relative

proportions of *cis*-1,4, *trans*-1,4 and 1,2 as the butadiene homopolymers, but showing a greater degree of variability. This may be due in part to the presence of a variety of diluents and rate-modifiers which influence the rates of the polymerization and possibly the actual polymerization temperatures.

This view is supported by the fact that polymers made at 30° without rate-retarding modifiers had butadiene configurations like those of polymers made at about 45°, i.e., lower percentage 1,2-configuration.

SUMMARY

The structures of various sodium and potassium-catalyzed butadiene polymers were determined from infrared absorption measurements. All of the polymers had a higher proportion of butadiene in the 1,2-configuration (45–80 per cent) than emulsion polybutadiene (18–23 per cent). Polybutadienes catalyzed by potassium had 15–20 per cent less butadiene in the 1,2-configuration than those in which sodium was the catalyst. When a mixture of sodium and potassium was used, the results were nearly the same as with the potassium catalyst alone. Polybutadienes made at 5° had 10 to 15 per cent more butadiene in the 1,2-configuration than those made at 45°. Diluent type had little or no effect on the structure of the polybutadienes. The butadiene portions of butadiene–styrene copolymers were found to have the same relative proportions of 1,2-, *cis*-1,4- and *trans*-1,4-configurations as the butadiene homopolymers. The second order transition temperature of sodium-catalyzed polybutadiene polymerized at 30° was –45°, whereas the 75° polybutadiene had a value of –64°.

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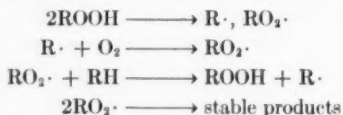
PRODUCTS OF OXIDATION OF AN OLEFIN STRUCTURALLY RELATED TO GR-S *

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The fields of rubber, plastics, surface coatings, and petroleum include a considerable portion of the industrial activity of the world, and in each of these industries oxidation is an important factor in product processing and in the properties of the final product. Information regarding the nature of the oxidation reactions observed in any of these fields can be applied in part to the others. Because of the complexity of the materials involved, it is frequently desirable to study pattern molecules of comparable structure and to seek to apply the knowledge obtained in this way to the more complex systems. This investigation is a part of a research program on the nature of the oxidation of natural and synthetic rubber and related materials. It is confined to the study of an olefin, 5-phenyl-2-pentene, which represents one of the possible repeating structural units of GR-S rubber.

There is considerable information in the literature regarding the probable mechanism of oxidation of hydrocarbons, both saturated and unsaturated. The oxidation of olefins, for example, has been studied extensively by workers in the laboratory of the British Rubber Producers' Research Association¹ and the following sequence of reactions for either thermal or photoxidation with molecular oxygen was proposed:



Tobolsky, Metz, and Mesrobian² have shown that reaction kinetics deduced from the above mechanism fit the data for the oxidation of dimethylcyclohexane, a saturated hydrocarbon, with molecular oxygen at 75° C, and no added catalyst.

In addition to these primary reactions, there is a host of secondary reactions leading to cross-linking, chain scission, and the formation of various oxygenated functional groups. Some of the ultimate products formed have been characterized for specific compounds and possible chemical mechanisms have been proposed³, but much more information will be required to establish the true nature of these reactions.

The object of the present study was to determine some of the products of the oxidation of an olefin structurally related to GR-S and to seek to interpret the data in terms of possible reactions involved. This paper is the third in a sequence of studies on this general subject⁴.

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EXPERIMENTAL PROCEDURES

Materials.—The 5-phenyl-2-pentene was prepared by the method of Lawrence and Shelton⁵, using γ -phenylpropyl bromide as the starting material. The final step involved the dehydrohalogenation of 5-phenyl-2-bromopentane. The olefin was purified by fractionation and it analyzed 97 to 99 per cent pure, based on unsaturation present. However, infrared data obtained in subsequent analysis of initial and oxidized samples (from a preliminary run at 90° C on a sample of 90 per cent purity) showed the presence of some terminal unsaturation. Thus the isomer, 5-phenyl-1-pentene was also present, and the relative amount, based on the infrared data, may have been as much as 20 per cent. (While this complicates the interpretation of the data, the mixture actually corresponds more closely to GR-S, since the isomer contains a terminal double bond like that of the side-chain vinyl groups formed to the extent of about 20 per cent by 1,2-polymerization of butadiene.)

Oxidations were carried out at two temperatures on samples of the following purities, based on unsaturation:

Oxidation temp. (° C)	Phenylpentene purity (%)
80°	97.3
100°	99.0

Apparatus and procedure.—The apparatus and procedure were the same as used by Warner and Shelton⁶. Oxygen was recycled through the liquid olefin at constant temperature ($\pm 0.3^\circ$ C) and atmospheric pressure. Water and carbon dioxide were absorbed continuously, and the volume of oxygen absorbed was measured periodically. Samples were removed for analysis at various stages of oxidation and stored under nitrogen at 0° C until the analyses were completed.

Analytical methods.—Peroxide was determined by the method of Wagner, Smith, and Peters⁷. The method is based on the liberation of bromine from potassium bromide and titration with sodium thiosulfate.

Warner's procedures⁶ were followed for determination of unsaturation by the bromide-bromate method and for determination of acid and ester by titrations before and after hydrolysis of the ester.

The method of Siggia⁸ for carbonyl oxygen was employed with some modification. The analysis depends on the quantitative reaction with hydroxylamine hydrochloride to liberate hydrochloric acid which is titrated. Calibration with acetophenone showed that 97.5 per cent could be accounted for by titration with alcoholic potassium hydroxide. However, color formed in the oxidized samples obscured the end point, so potentiometric titrations were used to obtain accurate results with the oxidized material. The procedure was also adapted to the use of 0.1-gram samples. Organic acids can be titrated independently and thus do not interfere. Aldehydes were detected qualitatively with fuchsin reagent (Schiff's test).

Water and carbon dioxide were absorbed by Drierite and Ascarite, respectively, in separate Nesbitt tubes.

Acids were partially separated and tentatively identified by the chromatographic procedure used by Marvel and coworkers⁹.

Alcohols were tested for by Siggia's procedure⁸, using acetylation, and epoxides were investigated by the method of Swern, Findley, Billen, and Scanlan¹⁰, using anhydrous hydrogen chloride in ether.

Infrared analyses were made using a Perkin-Elmer Model 12C spectrometer, operated with the automatic slit-width drive. A drop of sample was placed between two sodium chloride flats. A blank was run using a single flat.

There is always the possibility that certain functional groups may interfere in a procedure designed for another functional group. Certain of these possibilities were investigated. For example, the peroxide was assumed to be hydroperoxide, and a sample of 95 per cent di-*tert*-butyl peroxide analyzed only 0.52 percent hydroperoxide, indicating little interference from dialkyl peroxides. Both cumene hydroperoxide and di-*tert*-butyl peroxide were analyzed by the procedure for ester and the results showed 17.2 per cent of the hydroperoxide and 7.0 per cent of the dialkyl peroxide were consuming sodium hydroxide in the titration. Therefore, during the period of high hydroperoxide concentration, the ester values would be somewhat high.

DISCUSSION OF EXPERIMENTAL RESULTS

Oxygen absorption.—The oxygen-absorption curves obtained at 80° and 100° C for 5-phenyl-2-pentene are shown in Figure 1. The rate increases with temperature as expected, although the curve obtained at the higher temperature

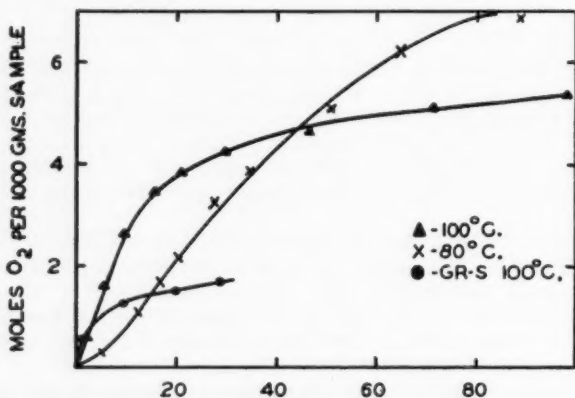


FIG. 1.—Comparison of oxygen absorption curves for 5-phenyl-2-pentene and uninhibited GR-S polymer.

leveled off at a lower stage of oxidation. The oxygen-absorption data obtained at 100° C with an unshortstopped, unstabilized, extracted GR-S polymer in a prior study¹¹ is also plotted in Figure 1 for comparison. The initial rate of oxidation was similar to that of the 5-phenyl-2-pentene at the same temperature, but the curve leveled off at a much lower value. The oxidized GR-S sample showed evidence of the formation of a hard surface layer which could account for the lowered rate as a result of limitation by rate of diffusion of oxygen into the sample.

Hydroperoxide formation.—The concentration of hydroperoxide is plotted on a mole basis in Figure 2 against oxygen absorbed. The maximum concentration is considerably higher at the lower temperature of oxidation. A maximum of nearly 0.8 mole of hydroperoxide per 1000 grams of sample was observed at 80° C at an oxygen absorption of approximately 3 moles of oxygen.

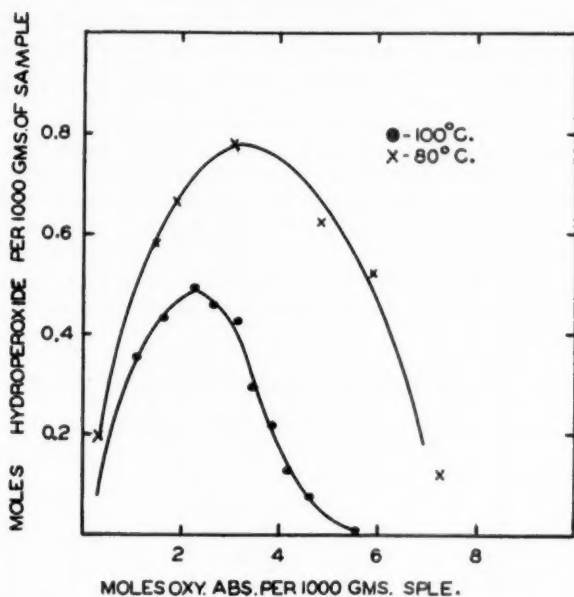


Fig. 2.—Hydroperoxide concentration at various stages of oxidation.

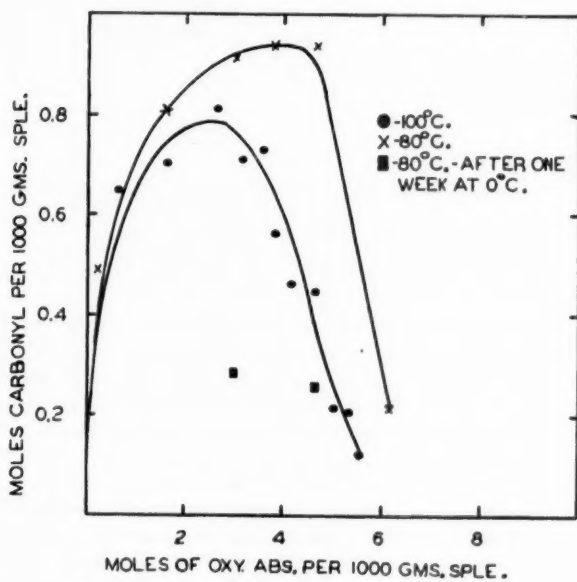


Fig. 3.—Carbonyl analysis at various stages of oxidation.

At 100° C the maximum was reached at about 2 moles of oxygen per 1000 grams of sample and with a peroxide analysis of approximately 0.5 mole.

Carbonyl formation.—The carbonyl concentrations observed at 80° and 100° C are plotted in Figure 3 on a mole basis against oxygen absorbed. The curves follow a similar pattern to the hydroperoxide curves, with the carbonyl maxima at slightly higher stages of oxidation (3 moles of oxygen per 1000 grams at 100° C and 4 moles at 80° C), and with a higher maximum for the material oxidized at the lower temperature. These relationships suggest that carbonyl is being formed from the peroxide and that the carbonyl is oxidized in turn to other products. The fact that carbonyl is subject to further oxidation is also shown by the fact that a sample stored at 0° C for a week gave a much lower value for carbonyl on subsequent analysis, as indicated by the extra points plotted in Figure 3.

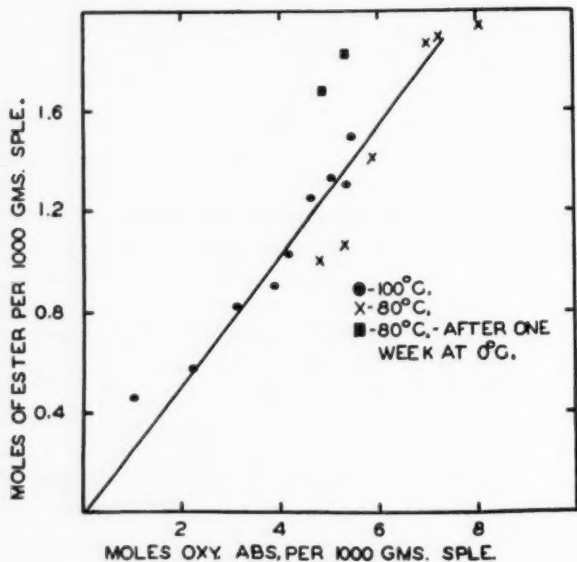


FIG. 4.—Ester formation at various stages of oxidation.

The procedure used for carbonyl determination would detect both aldehyde and ketone groups. Qualitative tests for aldehyde showed that they were present up to the 64th hour at 80° C, but no aldehydes were detected in the samples oxidized at 100° C. Apparently aldehydes are formed, but quickly oxidize to acids, and consequently the carbonyl values may be regarded as representing ketone groups.

Ester formation.—The formation of esters is plotted in Figure 4 on a mole basis as a function of oxygen absorbed. The relationship is nearly linear with the formation of 1 mole of ester during the absorption of 4 moles of oxygen at 100° C. The ester concentration formed at 80° C is slightly lower at equal stages of oxygen absorption. Oxidized samples stored for 11 days at 0° C and

then analyzed demonstrated that a marked increase in ester concentration had taken place on standing. These data are also plotted in Figure 4.

The relationships between peroxide, carbonyl, and ester concentrations are shown in Figures 5 and 6 for 80° and 100° C oxidations, respectively. The peroxide and carbonyl curves exhibit similar maxima, but the ester content continues to increase. However, the sum of ester plus carbonyl is essentially constant in the region where carbonyl is decreasing and ester is increasing. These data indicate that carbonyl is being converted to ester and that this reaction, rather than esterification of alcohols and acids, may be the main source of esters formed under these conditions. The observed decrease in carbonyl and increase in ester concentrations of oxidized samples stored at 0° C, as noted in Figures 3 and 4, also support this hypothesis.

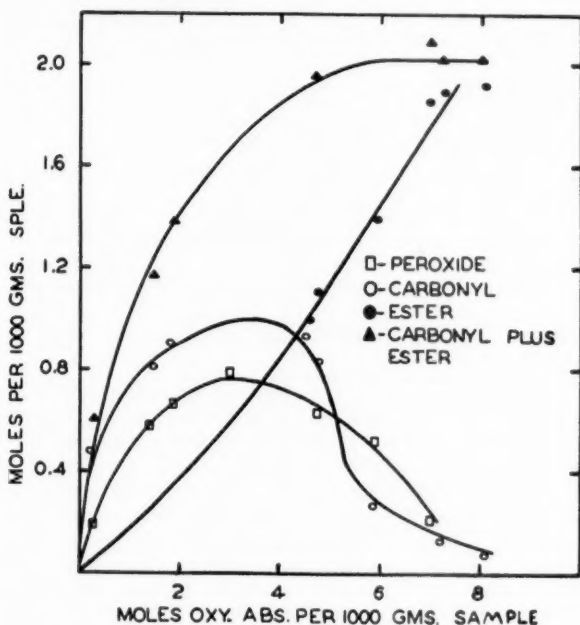


Fig. 5.—Concentrations of peroxide, carbonyl, and ester as a function of oxygen absorbed at 80° C.

The conversion of ketones to esters in the presence of peracids has been observed by other workers. For example, α , β -unsaturated ketones were converted to enol esters in the presence of peracetic acid¹². Peracids are probably present in the oxidation mixture as intermediates in the oxidation of aldehydes to acids. It is also possible that peroxides could effect the transformation. (This reaction is being investigated at the present time.)

Epoxide formation.—Epoxide analyses were run on the sample from the 100° C oxidation. α , β -Unsaturated ketones and esters are among the compounds which interfere in this procedure, since they tend to add anhydrous hydrogen chloride. Calibration of the procedure with known compounds con-

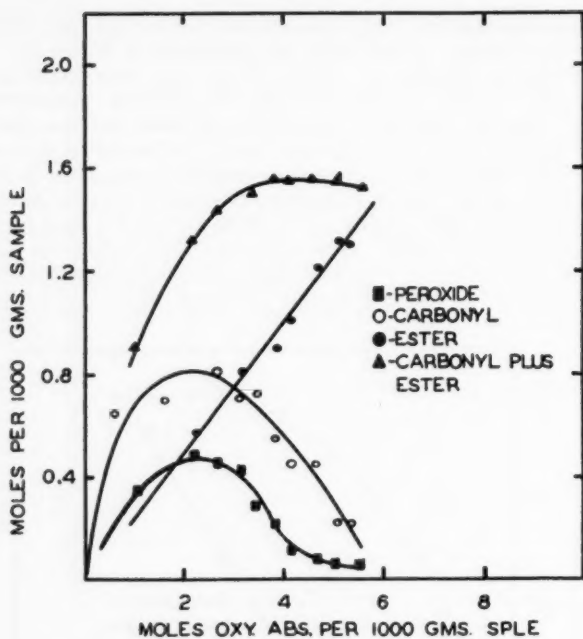


Fig. 6.—Concentrations of peroxide, carbonyl, and ester as a function of oxygen absorbed at 100° C.

firmed that these materials do react, but not quantitatively. The epoxide analyses in Table I are thus high. Correcting the values by subtracting the equivalent of (carbonyl + ester/2), which is the maximum interference if these groups reacted quantitatively, gives a minimum value for the epoxide concentration. The actual interference based on the observed behavior of mesityl oxide, crotonaldehyde, ethyl cinnamate, and ethyl maleate would be less than half the maximum. Thus a small amount of epoxide, about 1 per cent oxygen as weight per cent of sample, was apparently present. Reaction of epoxide with acid would be another possible source of ester in the oxidized material.

Unsaturation depletion.—The change in unsaturation with oxygen absorption is plotted on a mole basis in Figure 7. The data indicate a nearly constant relationship, although the change was somewhat greater in the early stages of oxidation and somewhat less in the later stages. The ratio of moles unsaturation lost to moles oxygen absorbed approximates a one-to-one relationship, but

TABLE I
EPOXIDE ANALYSES

Hours of oxidation at 100° C	Epoxide analysis (wt. % O ₂)	(Carbonyl + ester/2) (wt. % O ₂)	Minimum epoxide concn. (wt. % O ₂)
4	2.1	1.8	0.3
6	2.5	2.0	0.5
13	2.6	2.4	0.2
71.5	3.0	2.3	0.7

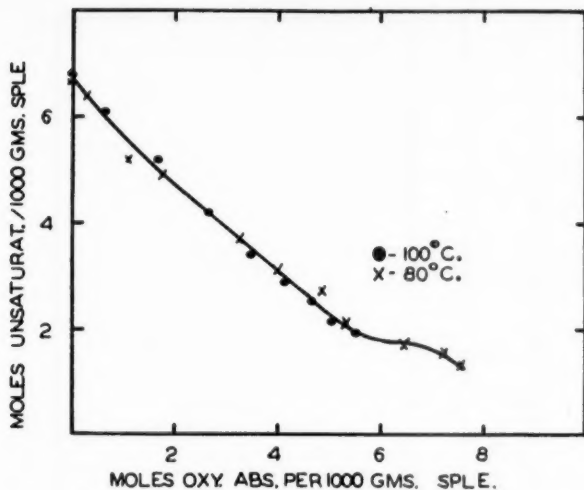


FIG. 7.—Changes in unsaturation with oxygen absorbed.

this should not be interpreted as evidence for direct oxygen attack at the double bond. Most of the decrease in unsaturation must be attributed to oxygen-induced polymerization, rather than to direct saturation with oxygen, since the sum of the oxygen accounted for by determination of the major oxygenated products (peroxide, carbonyl, ester, acid, carbon dioxide, and water) was sufficient to account for nearly all of the oxygen absorbed.

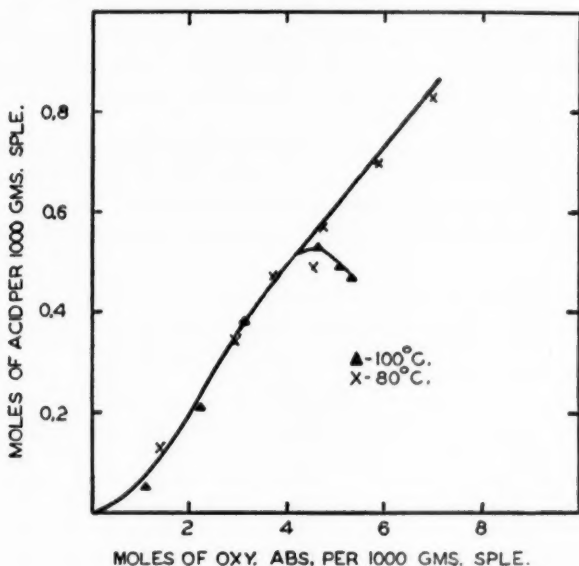


FIG. 8.—Acid formation at various stages of oxidation.

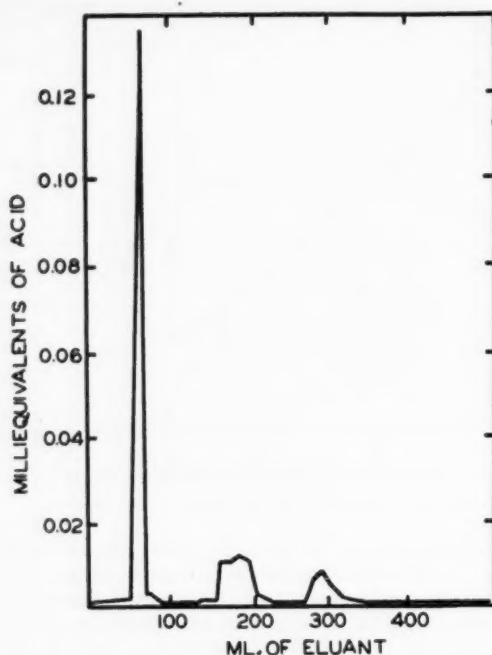


Fig. 9—Chromatogram for total acids in 5-phenyl-2-pentene oxidized at 80° C.

Acid formation and chromatographic analysis.—The formation of acids is plotted in Figure 8 as a function of oxygen absorbed. The relationship is nearly linear and data for the two temperatures coincide up to the point where the curve obtained at 100° C levels off.

The chromatographic procedure of Marvel and coworkers⁹ was employed to study the nature of the acids formed in the 80° C oxidation. Analyses were run both before and after hydrolysis of the esters present. A typical chromatogram is shown in Figure 9. The peaks correspond to certain acids and groups

TABLE II
CHROMATOGRAPHIC ANALYSIS FOR ACIDS
(Oxidation of 5-phenyl-2-pentene at 80° C)

Acid	Calibration absorption band (cc. Eluant)	Analysis	
		Free acids	Total acids
Crotonic	50	x	x
Phenylacetic	60	x	x
Phenylpropionic	60	x	x
Benzoic	160	x	x
Acrylic	170	x	x
Acetic	200	—	x
Formic	290	—	x

of acids. Known samples of the acids which appeared to be present were used to calibrate the procedure as shown in Table II, using butanol in chloroform as the eluant. Formic, acetic, acrylic, and benzoic acids were identified in this way in the product of the 80° C oxidation. Formic and acetic acids were detected only after hydrolysis, and thus were apparently present mainly as esters. The group of acids at 50 to 60 cc. of eluant was also studied, using ethyl alcohol in chloroform as the eluant, which spreads the group out somewhat. Only a trace of crotonic acid and a little more phenylacetic acid was indicated, with phenylpropionic acid being the major component of the group. This acid could be obtained by direct oxidative scission of 5-phenyl-2-pentene at the double bond or it could arise in part from the 5-phenyl-1-pentene isomer by way of ketone and ester.

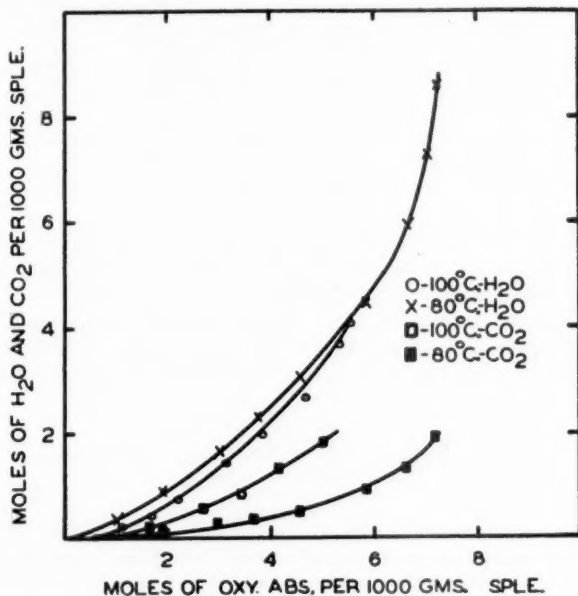


FIG. 10.—Formation of water and carbon dioxide at various stages of oxidation.

Water and carbon dioxide formation.—The formation of water and carbon dioxide is plotted on a mole basis in Figure 10 as a function of oxygen absorbed. The water liberated at 80° and 100° C in the oxidation of 5-phenyl-2-pentene was about the same for a given absorption of oxygen, but about twice as much carbon dioxide was liberated at the higher temperature.

Increasing amounts of water and carbon dioxide were liberated in the later stages of oxidation. For example, at 80° C the breaks in the curves come at about 6 moles of oxygen absorbed per 1000 grams of sample. This corresponds to about 65 hours and coincides with the time at which the oxygen-absorption curve leveled off. Beyond this point most of the oxygen consumed can be accounted for by the liberation of an equivalent amount of water and carbon dioxide.

Oxygen balances.—The oxygen balances obtained at various stages of oxidation at 80° C are shown in Table III. Similar data obtained from the oxidation at 100° C are shown in Table IV. In most cases, the analyses accounted for somewhat more oxygen than was absorbed. This was particularly true in the early stages, and was probably caused in part by hydroperoxide contributing to values obtained in the ester analysis and to similar duplication in other

TABLE III
OXYGEN BALANCE (80° C OXIDATION) AS WEIGHT PER CENT OF SAMPLE

	Hours of oxidation						
	5½	12½	20½	34½	50½	64½	89½
Ester	0.40	0.95	1.55	2.60	3.60	4.50	5.55
Acid	0.05	0.30	0.60	1.25	1.80	2.30	2.60
Peroxide	0.65	1.50	2.12	2.45	2.05	1.65	1.10
Carbonyl	0.80	1.20	1.40	1.50	1.35	0.40	0.33
CO ₂	0.09	0.09	0.47	1.09	1.93	2.86	4.18
H ₂ O	0.58	0.58	1.47	3.81	5.83	7.20	9.50
Total	2.57	4.62	7.61	12.69	16.56	18.91	22.26
O ₂ absorbed	0.93	3.49	6.04	11.84	15.13	18.79	21.30

analyses. In general, the balance was good, indicating that most of the oxygen was accounted for. Ether oxygen was not measured and the small amount of epoxide was not included in the balance.

Infrared analyses.—Examination of the infrared spectrograms obtained with samples of oxidized 5-phenyl-2-pentene and correlation with known band absorptions showed the presence of the groups listed in Table V. These data

TABLE IV
OXYGEN BALANCE (100° C OXIDATION) AS WEIGHT PER CENT OF SAMPLE

	Hours of oxidation						
	2	6	10	16	30	47	71.5
Ester	0.50	1.75	2.30	2.75	3.50	4.00	4.20
Acid	0.00	0.40	1.00	1.35	1.68	1.70	1.60
Peroxide	0.50	1.35	1.50	1.05	0.40	0.20	0.16
Carbonyl	1.00	1.15	1.20	1.10	0.80	0.70	0.40
CO ₂	0.20	0.60	1.10	1.80	3.20	4.20	5.20
H ₂ O	0.10	0.60	1.50	2.80	3.50	4.20	5.00
Total	2.30	5.85	8.60	10.85	13.80	15.00	16.56
O ₂ absorbed	1.50	5.00	8.50	11.00	13.20	14.50	16.10

were obtained in a preliminary run at 90° C on a sample of lower purity (90 per cent based on analysis for unsaturation).

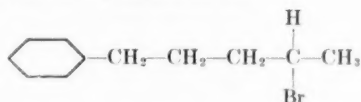
In addition to the 2.95-micron absorption band for hydroperoxides, the only other observable band was possibly at 11.9 microns¹³. However, the epoxy group¹³ should also yield an absorption band at this position. The other epoxy absorption band at 11.2 microns was obscured by the HC=CH₂ absorption at 11.0 microns.

The C=O absorption band occurs at 5.5 to 6.2 microns. Esters, acids, and ketones would be expected to absorb in this region. In correlation with chemical analyses, it was not possible to identify the shift in absorption caused by the progressive formation and depletion of the ketone carbonyl group and the formation of acids and esters. Band shifts caused by α , β -unsaturation were probably partly responsible for this.

TABLE V
INFRARED ABSORPTION BANDS

Group	Position (microns)
OH (probably hydrogen-bonded hydroperoxide)	2.95
C=O	5.5-6.2
—HC=CH—	10.35
—HC=CH ₂	11.0
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{—CH—CH—} \end{array}$	12.0
—O—O—H	12.0

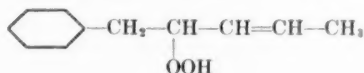
Since the thickness of the sample used in the spectrometer varied from sample to sample, it was necessary to correlate the sample thicknesses by assuming a constant absorption for the phenyl group. Based on this adjustment, the ratio of internal double bonds to vinyl groups decreased with oxidation time, indicating a greater stability for the vinyl group. The vinyl group was formed by partial dehydrohalogenation of the



in the direction of the terminal carbon atom, and the resulting isomer was not completely removed in the purification of the 5-phenyl-2-pentene. Based on the infrared data, the concentration of vinyl groups could account for as much as 20 per cent of the unsaturation present in the original sample. The concentration may not have been as great in the more highly purified samples.

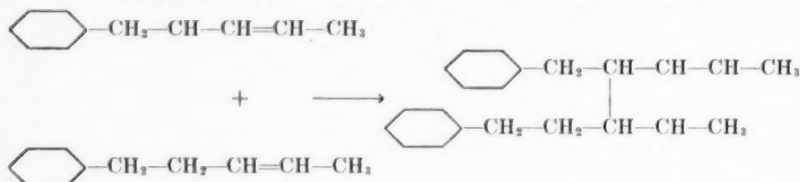
SUMMARY OF INDICATED REACTIONS

The formation of hydroperoxide as a primary oxidation product of an autocatalytic free-radical chain mechanism appears to be well established¹⁴. Initiation in the autocatalytic stage appears to be mainly by decomposition of hydroperoxide to form free radicals, but direct attack of oxygen at both the double bond and the α -methylene group is probably also involved. In the case of 5-phenyl-2-pentene, the most important primary oxidation product would thus be:



The decomposition of hydroperoxide not only initiates further oxidation, but also leads to a number of secondary oxidation products. In the presence of free radicals, polymerization of an olefin is to be expected. Either $R\cdot$, $RO\cdot$, or $RO_2\cdot$ could add to a double bond to initiate polymerization by a free-radical mechanism. However, most of the unsaturation loss observed apparently involved addition of hydrocarbon free radicals, since the oxygen absorbed was accounted for in oxygenated functional groups other than ether or dialkyl peroxide.

The following reaction for 5-phenyl-2-pentene illustrates a probable method of cross linking in the oxidation of GR-S and other comparable materials:



Some of the probable secondary oxidation reactions, based on the oxidation products observed in this study, are summarized in Figure 11. Cleavage of the hydroperoxide at the O—O bond would give an $RO\cdot$ radical which could lead to

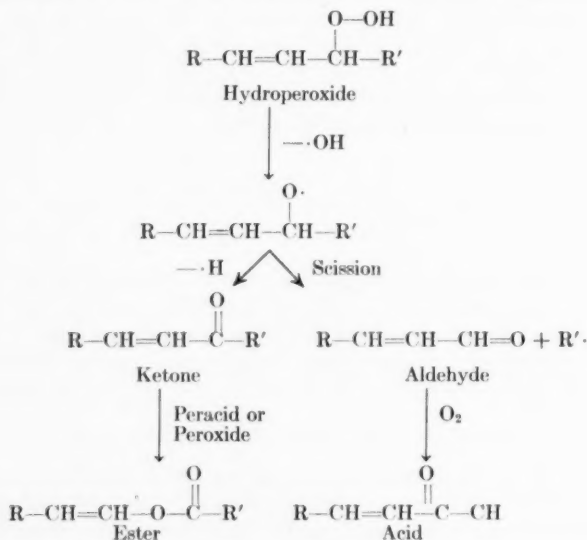
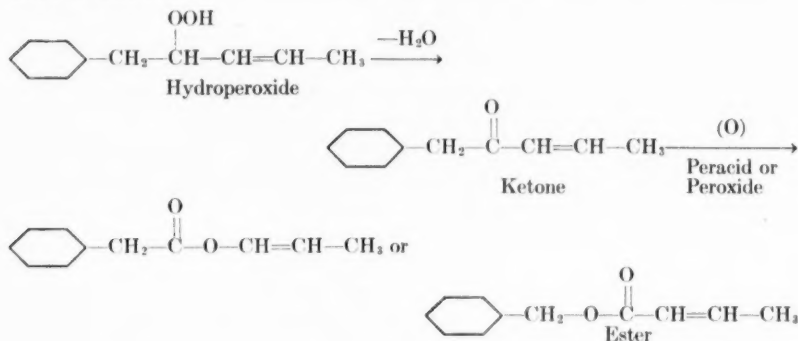


FIG. 11.—Formation of secondary products by peroxide decomposition and subsequent reactions.

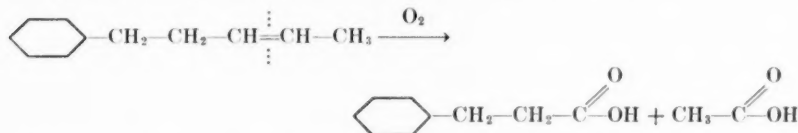
either carbonyl by completion of the dehydration of the hydroperoxide or to chain scission by withdrawal of an electron from an adjacent bond to form a free radical and an aldehyde. The aldehyde would be converted to acid by subsequent oxidation. The ketone could be converted to ester by oxidation with either peracid¹², formed by oxidation of aldehyde, or possibly by peroxide.

In the case of 5-phenyl-2-pentene, reactions leading to ester may be formulated as follows:



Ester could also be formed by reaction of epoxide with acid.

Chain scission may occur either by decomposition of radicals, as suggested in Figure 11, or by direct oxidative scission of the double bond.



It is necessary to take into account both phenylpentene isomers and both mechanisms to account for the acids observed in this study.

Any alcohols formed as intermediates are apparently either dehydrated to olefins or esterified by the excess of acids, since no free alcohols were detected. The continuous removal of water from the system would tend to drive both reactions to completion.

Water and carbon dioxide can be accounted for by such reactions as dehydration of peroxide, decarboxylation of acids, and complete oxidation of fragments such as formic acid.

Reactions similar to those observed with 5-phenyl-2-pentene no doubt occur in GR-S and other related materials. The limitations inherent in the use of pattern molecules must be taken into account, however, in interpreting the significance of the data when applied to more complex systems.

ACKNOWLEDGMENT

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EFFECT OF ASSOCIATED SALTS ON THE POLYMERIZATION OF BUTADIENE BY ORGANOSODIUM REAGENTS *

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The polymerization of dienes by sodium metal is probably the oldest known method for producing synthetic rubber. A course for the reaction has been traced by Ziegler and co-workers through the 1,4-disodium-2-butene intermediate and thence as an organosodium reagent through a series of adduct compounds to a rubber which is primarily the result of 1,2-rather than the 1,4-chain growth required to make it relatively similar to Hevea. The same type of polymer is obtained if the first stage with sodium metal is omitted and any active organosodium reagent is substituted as the starting agent. This sodium process gives an unsatisfactory product when used with butadiene and isoprene, but in World War I the Germans applied it to 2,3-dimethylbutadiene to give a moderately suitable polymer. Subsequently the emulsion process was developed and yielded a better type of product in which around 80 per cent of the butadiene was joined end to end, that is, 1,4-. The present synthetic rubber for general use belongs with the emulsion class. All things considered, the rubber made by the emulsion process is distinctly different from that by the sodium method, so much so that an examination of physical properties alone serves easily to differentiate the two materials, even if their sources are unknown.

The purpose of this paper is to point out how the sodium process as practiced with an organosodium reagent as the starting point can be altered so as to produce differences which are even greater than the significant ones found between the sodium and emulsion types of polymerization. The change is brought about by association of the organosodium compound—a reagent insoluble in the reaction media—with other solid sodium salts of a less reactive type, even of such slight reactivity as found in sodium chloride. In proper kind and proportion, however, the effect of the additional salts can be astonishing, both as to the rate of polymerization and the structure of the polymer. The particular combination which has given the most outstanding result is allylsodium associated with sodium isopropoxide and sodium chloride and is known as an alfin catalyst¹. Allylsodium by itself is slow-acting and yields a polymer having an intrinsic viscosity less than 1 and having around 70 per cent external double bonds, the product of 1,2-addition. By the presence of the two associated salts the same quantity of allylsodium achieves polymerization at enormous speeds to polymers with intrinsic viscosities of 12 or more with 70 to 80 per cent 1,4-structure. Emulsion polymerization can scarcely achieve intrinsic viscosities much above 3.

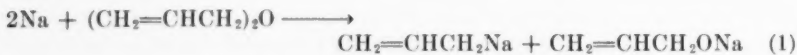
* Reprinted from *Industrial and Engineering Chemistry*, Vol. 44, No. 12, pages 2876-2882, December 1952.

The full scope of these changes, the exact composition of the catalyst, and the degree to which the behavior of an organosodium reagent is controlled by the associated salts were not at first realized. Indeed, in the beginning, the name alfin was given on the assumption that only two components, the salt of an alcohol and an olefin, were necessary². However, as this paper will show, sodium chloride is as essential as the other two salts. Substitution of sodium chloride by many other related salts is possible. Each single salt of the three component mixtures has some influence, but all three are needed to obtain the effects achieved as an alfin catalyst. The cation required for these salts is equally specific, sodium being of prime importance. A limited substitution of sodium by potassium is possible and, in a few cases, may cause a faster rate of polymerization. The lithium ion cannot be used in general without impairment of activity, although in some cases its bad influence can be partly compensated by association with a large anion, such as the iodide in place of chloride.

As the organosodium reagent becomes more active and effective, it also becomes more specific. For instance, an ordinary organosodium compound without high specificity causes styrene to polymerize faster than butadiene, whereas the alfin catalyst causes butadiene to polymerize much faster than styrene³. A given quantity of catalyst has a great effect on butadiene, much less on isoprene, and scarcely any on 2,3-dimethylbutadiene⁴, the monomer for the old methyl rubber. This high specificity is an important feature of this development where, for the first time, a clear demonstration has been possible in a field where specificity is sorely needed, because it is apparent that if the synthesis of polydienes of specific structures, such as are found in Hevea or balata, is ever to be achieved in the laboratory or plant the development of highly specific catalysts is essential. The three-component alfin catalyst illustrates unusually well the degree that specific components of the reagent contribute to specific properties of the polymer and shows the way to further study of this method of controlling polymerization.

PREPARATION OF CATALYST

The alfin catalyst⁵ has hitherto been prepared by two different methods. In one (A) amylsodium reacts with diisopropyl ether and in the other (B) amylsodium reacts with propylene in the presence of sodium isopropoxide. In both cases sodium chloride is in the catalyst because it is associated with amylsodium, having been formed during the reaction of amyl chloride with sodium. An alternative method produces allylsodium free from sodium chloride and sodium isopropoxide by a cleavage⁶ (see Equation 1) of diallyl ether with an alkali metal. It is designated as method C and was used in the present study.



Sodium allyloxide was thereby introduced, but had no major adverse effect as found by independent tests where the salt was made separately from sodium and allyl alcohol and was then mixed with an alfin catalyst of known activity and allowed to age over 3 months. However, its presence during a preparation of catalyst by method B decreased the formation of allylsodium because the sodium allyloxide was metalated preferentially and then underwent dimerization or polymerization.

The allylsodium prepared by method C was used to polymerize butadiene in the absence and presence of either or both sodium isopropoxide and sodium chloride. When polymerization was of a nonalfin type, the most easily observed features were that the percentage conversion by a given quantity of reagent was low, even though the time was long, and that the intrinsic viscosity of the polymer was low, in these tests less than two. If the alfin type of polymerization prevailed, the polymerization was faster, with well over half being completed in a half hour, and the corresponding intrinsic viscosity was higher, usually above four and reaching to ten or more.

These features were easily perceived in any good alfin agent. However, some mixtures of salts contained the essential ingredients, but showed no alfin characteristics because the sodium chloride was the commercial granular material and too coarse to be incorporated properly with the other salts. Yet even

TABLE I
EFFECT OF SALTS ON THE POLYMERIZATION OF BUTADIENE BY MEANS
OF ALLYLSODIUM PREPARED BY CLEAVAGE OF DIALLYL ETHER

Reagent no.	Salts present ^a		Polymer- ization time (min.)	Yield ^c (%)	Intrinsic viscosity	Gel (%)	Pptn. test ^d
	During cleavage	After cleavage ^b					
1	RONa	—	30	Low	Low	—	Neg.
2	NaCl(w)	—	480	14	0.4	3	Neg.
3	RONa-NaCl(w)	—	30	59	20.5	33	Pos.
4	RONa-NaCl(w)	—	30	40	20.5	19	Pos.
5	RONa	—	240	3	1.5	43	Neg.
6	RONa	NaCl(w)	30	21	7.9	51	Pos.
7	RONa	NaCl(g)	240	3	0.3	41	Pos.
8	RONa-NaCl(g)	—	230	9	8.9	20	—
9	RONa-NaCl(g)	—	150	Low	Low	—	Pos.
10	RONa-NaCl(g)	—	180	2	2.4	23	Pos.
11	RONa-NaCl(g)	—	240	11	2.0	27	Pos.
12	RONa-NaCl(g)	—	240	3	1.6	49	Pos.
13	RONa-NaBr(w)	—	30	18	9.6	22	—
14	RONa-NaI(w)	—	30	71	17.5	41	—

^a R signifies the isopropyl group; the letters w and g in parentheses indicate that the sodium chloride was prepared by a Wurtz reaction or was the granular material obtained from commercial sources.

^b The salt and sodium reagent were stirred together vigorously in the high-speed stirring apparatus.

^c The yield is the percentage of polybutadiene obtained when 10 cc. of the reagent acts on 30 cc. of butadiene in 200 cc. of pentane.

^d With iodine monochloride; not attempted on some of the polymers.

in these cases, a little alfin product was detected by a precipitation test (to be described later) with iodine monochloride.

Table I shows the activity of the reagents prepared by this cleavage. The first two and reagent 5 contained sodium isopropoxide or sodium chloride, but not both, and caused no alfin polymerization. The third and fourth contained both salts, the sodium chloride being the finely divided material from a Wurtz reaction, and showed alfin character clearly. Reagent 5, a repeat of reagent 1, was inactive until sodium chloride from a Wurtz reaction was stirred into the mixture to make reagent 6. A similar attempt with granular sodium chloride gave reagent 7, which had so little alfin activity that only the iodine monochloride precipitation test revealed it. Reagents 8 to 12 also contained commercial sodium chloride, and each corresponding polymer showed a precipitate with the iodine monochloride reagent, even though the other tests usually gave unsatisfactory characterizations. The last two reagents were made with Wurtz sodium halides. Their alfin characters were easily discerned. These

results certify the need for the third salt in the alfin catalyst and the necessity for its thorough incorporation if the reagent is to be good.

The use of granular sodium chloride was next improved and numerous commercial halide salts were found to replace sodium chloride. The method was to prepare the isopropoxide from alcohol and sodium in the presence of the halide and stir the mixture for 3 hours before incorporation in the cleavage reaction,

TABLE II
HALIDE SALTS AS COMPONENTS OF AN ALFIN CATALYST

Prepn. no.	Salt	Bond dist. A.	Cat. used (cc.)	Polymer		Intrinsic viscosity	Gel (%)	Alfin activity*
				Yield (%)	Yield per cc. (%)			
1	LiF	2.01	25	0.5	0.02	Low	—	N
2	NaF	2.31	25	0.4	0.02	0.6	30	N
3	NaF	2.31	25	0.5	0.02	0.6	36	N
4	NaF	2.31	25	0.7	0.04	0.6	53	N
5	LiCl	2.57	25	0.5	0.02	1.0	40	N
6	KF	2.67	10	0.4	0.04	0.9	13	N
6	KF	2.67	20	0.9	0.05	0.9	33	N
7	LiBr	2.75	25	0.3	0.1	2.4	24	N
8	LiBr	2.75	25	0.3	0.1	1.9	38	N
9	NaCl	2.81	10	7	0.7	8.3	5	G
9	NaCl	2.81	20	10	0.5	9.2	5	G
10	NaCl	2.81	10	4	0.4	9.3	46	F
10	NaCl	2.81	20	5	0.3	9.0	23	F
11	NaBr	2.98	10	13	1.3	10.7	4	VG
11	NaBr	2.98	20	18	0.9	10.0	5	G
12	CsF	3.01	10	1	0.1	4.0	71	P
12	CsF	3.01	25	3	0.1	4.7	81	P
13	LiI	3.02	10	5	0.5	10.0	36	G
13	LiI	3.02	25	14	0.6	9.7	41	G
14	KCl	3.14	10	16	1.6	12.0	16	VG
14	KCl	3.14	20	36	1.8	12.4	23	VG
15	NaI	3.23	10	5	0.5	9.4	8	G
15	NaI	3.23	20	10	0.5	8.6	8	G
16	KBr	3.29	25	2	0.1	4.9	49	P
17	KBr	3.29	10	13	1.3	8.4	15	VG
18	KI	3.53	25	1	0.04	4.2	72	VP
19	KI	3.53	10	2	0.2	9.3	62	P
19	KI	3.53	20	4	0.2	8.0	68	P
20	CsCl	2.06	10	4	0.4	3.4	71	F
20	CsCl	2.06	25	13	0.5	3.1	73	G
21	CsBr	2.14	10	5	0.5	4.7	66	G
21	CsBr	2.14	25	9	0.4	6.9	52	F

* The letters N, G, F, P, and VG refer, respectively, to none, good, fair, poor, and very good as judged by the percentage conversion.

all in the high-speed stirring apparatus⁷, which grinds as well as mixes. Table II lists these tests, except for the last two, in the order of increasing bond distance between the respective ions (the third column) because some physical factor seems important and bond distance can influence surface catalysis. The first 19 preparations are with similar salts, each having the sodium chloride type of cubic crystal structure. The last two have the cesium chloride structure.

All halide salts of the sodium chloride type with bond distance at 2.75 Å. and below failed to produce alfin catalysts, whereas those at 2.81 Å. (the value for sodium chloride) and above did form them. The best were in the range from 2.81 to 3.29 Å., although in uneven gradation. Potassium chloride, sodium bromide, potassium bromide, and sodium chloride were most effective approximately in order. At 3.53 Å., which is the value for potassium iodide, the activity was poor and one of the preparations was very unsatisfactory.

TABLE III
INFLUENCE OF PSEUDOHALIDES, MISCELLANEOUS SALTS, AND OTHER
SURFACES ON THE POLYMERIZATION ACTIVITY OF ALLYLSODIUM
TOWARD BUTADIENE

No.	Salt	Cat. used (cc.)	Polymer		Intrinsic viscosity	Gel (%)	Alfin activity ^a
			Yield (%)	Yield per cc. (%)			
1	NaCN	10	14	1.4	9.6	13	VG
		20	14	0.7	9.5	8	G
2	KCN	10	13	1.3	9.4	18	VG
		20	36	1.8	9.8	22	VG
3	NaSCN	10	31	3.1	13.8	45	E
		20	50	2.5	11.8	56	E
4	KSCN	10	40	4.0	13.9	20	E
		25	60	2.4	11.5	50	E
5	KCNO	10	2	0.2	2.9	54	N
		20	4	0.2	2.8	59	N
6	NaH	10	Low	—	Oil	—	N
7	NaOCH ₃	25	Low	—	Oil	—	N
8	NaOH	10	0.5	0.05	0.5	33	N
9	NaNO ₂	10	0.5	0.05	1.2	38	N
10	Na ₂ CO ₃	25	Low	—	Oil	—	N
11	K ₂ CO ₃	10	13	1.3	4.0	12	VG
		25	80	3.2	2.5	13	E
12	Na ₂ SO ₄	25	0.6	0.02	1.5	35	N
13	K ₂ SO ₄	25	Low	—	Oil	—	N
14	CaCl ₂	25	0.0	—	—	—	N
15	Alumina	35	0.1	0.10	0.3	22	N
16	Carbon ^b	25	0.2	0.01	0.4	3	N
17	Silica gel	25	0.9	0.04	0.5	45	N
18	Glass ^c	25	1.0	0.04	1.0	54	N

^a The letters have the same significance as in Table II. E means excellent; however the best of the catalysts made by this method (C) are inferior to those made by method B.

^b Merck's activated carbon.

^c Soft glass was powdered in a mortar with pestle.

The two cesium salts with cesium chloride structure (numbers 20 and 21) were much better than cesium fluoride (reagent 12) which has the sodium chloride cubic structure and is in the preferred range for salts of that type.

The tests were then extended to other salts and halides. As a class the pseudohalides (see Table III, numbers 1 to 5) and the thiocyanates were very good to fine. The thiocyanates have a rhombic structure and the potassium salt has a bond distance of 3.33 Å. The chemically active sodium hydride, sodium methoxide, and sodium hydroxide (numbers 6 to 8) created no alfin

activity. Therefore, ordinary chemical activity was not required in the third component. Only potassium carbonate of the miscellaneous salts tested in numbers 9 to 14 showed any alfin activity. Some of the ordinary type of sodium polymerization may have been present, because the intrinsic viscosity of the polymer was comparatively low and was much lower at high conversion. The common supports for catalysts tested in the last four experiments listed in the table failed to create activity as did sodium chloride. Specific ions are, therefore, required for alfin activity. The geometry of the surface seems important.

Tests with isoprene confirmed those with butadiene in that sodium chloride proved essential for alfin catalysis and sodium thiocyanate could replace the chloride (see Table IV), although in this case not so effectively because it was the coarse granular material and the chloride was the finely divided Wurtz product. Butadiene was polymerized about seven times faster than isoprene

TABLE IV
INFLUENCE OF A THIRD^a ACTIVE (ALFIN) SALT ON POLYMERIZATION
OF ISOPRENE AND BUTADIENE BY ALLYLSODIUM AND SODIUM
ISOPROPOXIDE

Diene	Third salt	Cat. ^b (cc.)	Time (hrs.)	Yield (%)	Yield/hr./cc. cat. used (%)	Comp. yield ^c	Intrinsic viscosity	Gel (%)
Isoprene	None	25	9	1.6	0.007	1	3.1	17
	None	25	18	3.2	0.007	1	—	—
	NaCl(w)	10	2.5	5.4	0.22	31	6.3	3
	NaSCN	10	2.5	0.4	0.02	3	—	—
	NaSCN	25	5.0	11.8	0.09	13	8.0	21
Butadiene	None	20	3.0	3.0	0.05	7	1.0	18
	NaCl(w)	10	0.5	46.0	9.2	1310	16.3	30
	NaSCN	10	0.5	31.0	6.3	900	13.8	45

^a Actually a fourth salt, sodium allyloxide, was present in all these tests.

^b Volume of catalyst used on 30 cc. of butadiene in 200 cc. of pentane.

^c Comparative yield based on the first two as 1.

by the ordinary sodium reagent and about 40 to 70 times faster by the alfin catalysts.

EFFECT OF THE CATION

The sodium cation is essential for alfin catalysis and potassium can replace sodium only in part. The tests were made by replacing one or more of the sodium salts by the corresponding potassium one in either method B or C (usually C) for preparing the catalyst. In addition to the criteria already described, several other features were used as rough guides for alfin catalysis. The viscosity of the polymer was independent of the monomer-catalyst ratio, whereas in nonalfin polymerization the usual rule of lower viscosity with more organo-sodium reagent held. The alfin polymers were only slightly soluble in pentane if at all under the conditions used, while the nonalfin polymers obtained under the conditions of these experiments were sticky oils that dissolved easily. In some cases both polymers were obtained from the same reaction and could be separated by their relative solubilities. The alfin polymerization was only moderately exothermic and no appreciable color change was observed during the reaction, whereas the nonalfin type was noticeably exothermic and the

TABLE V
 EFFECT OF CATION ON ALFIN CATALYSIS

No.	Prepn. method ^a	Cation ^b present with			Polymerization ^c		Type ^d obsvd. by
		Allyl	Iso-propoxide	Chloride	Alfin	Potas.	
1	C	Na	Na	K(w)	Y	N	1,2,4,5
2	C	Na	Na	K(g)	Y	N	1,2,4,5
3	B	Na	K	Na(w)	Y	Y	1,2,5
4	B	Na	K	Na(w)	Y	N	1,2,4,5
5	C	Na	K	Na(g)	Y	Y	1,2,5
6	C	K	Na	Na	N	Y	2,5
7	C	Na	K	K	N	Y	1,2,3,5
8	C	K	Na	K	N	Y	2,5
9	C	K	K	Na	N	Y	1,2,5
10 ^e	C	K	K	K	N	Y	1,2,3,4,5

^a The letters designate the method of preparing the catalyst as described at the beginning of this paper.

^b The letters w and g in parentheses refer to the source of the halide salt as given in Table I.

^c Y signifies yes, N means none. The nonalfin type is designated as Potas.

^d Observations were made of the following five points on alfin-type polymerization: (1) relative insolubility of the polymer in pentane; (2) high viscosity of the polymer; (3) iodine monochloride precipitation of the polymer; (4) viscosity of polymer largely independent of monomer/catalyst ratio; (5) moderate exothermic character and absence of color change, blue to pea-green to brown.

^e Some metallic potassium was present in this reagent.

color changed from blue to pea-green to brown as it does when amylsodium is the reagent.

By these criteria the sodium cation in the isopropoxide salt or the halide salt was found to be replaceable separately (Table V, numbers 1 to 5) by potassium but not in both salts simultaneously (number 7). Allylsodium could not be replaced by allylpotassium (number 6) in spite of the fact that ion interchange in the aggregate might occur and probably does very slowly, earlier experiments⁸ having shown that time often alters the activity of these reagents. The replacement of sodium by potassium in all three salts produced a fast-acting reagent (see also Table VIII), but the polymer therefrom had a low intrinsic viscosity and was nonalfin by every test.

The lithium ion usually destroyed the alfin catalyst when only a moderate amount was present. This fact was shown in Table II for the halides, and also in two different series where lithium isopropoxide was incorporated in an alfin catalyst which otherwise would have been very active. The activity decreased and disappeared when as many moles of lithium isopropoxide had been added as there were moles of sodium isopropoxide in the catalyst. The same test with

 TABLE VI
 EFFECT OF ADDITIONAL ALKOXIDES OVER THAT NEEDED TO MAKE THE RATIO OF ALLYLSODIUM TO SODIUM ISOPROPOXIDE APPROXIMATELY 1:1

Excess alkoxide ^a	Cat. concn. ^b	Yield ^c (%)	Yield per mg. of cat. (%)	Intrinsic viscosity	Gel (%)
None	0.19	38	40	13.1	16
sio-NaOC ₃ H ₇	0.13	63	96	15.4	13
tert-NaOC ₃ H ₁₁	0.13	30 ^d	23	15.9	51
iso-KOC ₃ H ₇	0.20	31	31	16.3	47
iso-LiOC ₃ H ₇	0.20	0			

^a In all cases the alkoxide in excess of that used in the first or control experiment was the same.

^b This value is given as milliequivalents of allylsodium per milliliter of suspension and the amount is an average of yields which have been obtained in a number of preparations.

^c Yield of polymer caused by 5 cc. of catalyst suspension.

^d 10 ml. of catalyst used in this experiment.

sodium or potassium isopropoxide caused no deterioration in activity (see Tables VI and VII).

INFLUENCE OF SALTS ON THE POSITION OF THE DOUBLE BONDS IN THE POLYMERS

The salts associated with the organosodium reagent affected the number of external double bonds, that is, the side vinyl groups produced by 1,2-polymerization, irrespective of whether polymerization was of the alfin type or not. Iodine monochloride was used for measuring total unsaturation and perbenzoic acid for the external double bonds, each according to the procedures of Kolthoff and coworkers⁹. The polymers were prepared by a miscellaneous group of reagents which had all or some of the components of the alfin catalyst. The results are listed in Table VIII in the order of increasing percentage of external double bonds.

The lowest percentage was 25 where all the components needed for the alfin catalyst were present. The first five reagents have in common the same anions, except that the *n*-propoxide was substituted for the isopropoxide in number 3. Their average percentage for the external bonds is 34. For numbers 6 to 11,

TABLE VII
EFFECT OF LITHIUM ISOPROPOXIDE ON THE ACTIVITY
OF AN ALFIN CATALYST

Excess ^a	Isopropoxide (mole)	Polymerization	
		Cat. (cc.)	Yield (%)
Lithium	0.113	3	54
	0.113	10	93
	0.225	20	0
Sodium	0.225	3	74
	1.125	3	24
	1.125	10	100

^a Excess alkoxide added over that formed by addition of 0.225 mole of 2-propanol to standard preparation from 1 gram atom of sodium.

only two of the salts needed for the alfin catalyst were present. As a class the external double bond percentage is higher; the average is 43. The last two reagents have only one of the alfin salts or have a limited quantity of the second salt and the average external double bond is 52 per cent. The highest is 61 per cent. This last value is near that credited¹⁰ to the usual type of sodium polymerization. Similar results were found with isoprene, where the percentage of external double bonds was lower. The two reagents (Table IX) which had the three salts that were in alfin catalysts had the lower percentages; the one with only two salts of the alfin system had a higher value.

It is clear, therefore, that salts affect the number of external double bonds. The components of the alfin catalyst have so far been responsible for producing polymers with the lowest percentage of 1,2-structure, but alfin catalysis is not essential for a low value, as shown by numbers 3 and 5 of Table VIII. A combination of three salts seems more effective than two.

This influence of salts in polymerization may, at first, seem strange. A salt effect is, however, the rule even in the simplest reactions of organosodium reagents. In the alkylation of toluene, the yield of *n*-hexylbenzene was more

TABLE VIII

INFLUENCE OF SALTS ON THE POLYMERIZATION OF BUTADIENE AND THE UNSATURATION OF THE POLYMER

No.	Components ^a in reagent			No. of alfin salts present	Method of prepn.	Yield (%)	Intrinsic viscosity	Gel (%)	Total unsatn. (%)	External double bonds (%)
	RM	ROM	MX							
1	Al-Na	Na(iso)	NaCl	3	B	28	11.6	7	100 ^b	25
2	Al-Na	Na(iso)	NaCl	3	B	65	12.6	39	98.9 ^c	28 ^{c,d}
3	Al-Na	Na(n)	NaCl	2 ^e	B	6	1.2	68	77	32
4	Al-Na	Na(iso)	NaCl	3	C	14	1.8	11	75	37
5	Al-K	K(iso)	KCl	3	C	95	1.8	4	85	37,41
6	Am-Na	Na(iso)	NaCl ^f	2	B	8	1.0	7	72	40
7	Al-Na	Na(iso)	LiBr	2 ^g	C	7	0.6	4	73	42
8	Al-Na	—	NaCl	2	B	14	0.4	3	73	44
9	Al-Na	Na(iso)	—	2	C	16	0.8	2	77	44
10	Al-Na	Na(iso)	NaOH	2	C	5	0.8	4	73	44
11	Al-Na	Na(iso)	—	2	C	4	0.4	2	81	47
12	Al-Na ^h	—	NaCl	2	B	4	0.5	6	83	53
	Am-Na	—	NaCl	1	—	—	—	—	—	—
13	Am-Na	—	NaCl	1	B	45	0.7	4	83	61

^a M refers to the metal cation, Al to allyl, Am to amyl, and R to a propyl radical which is iso or normal as indicated in the column.

^b This value was assumed because the iodine monochloride reagent caused precipitation that made the test unreliable.

^c This value was taken from the literature¹⁴.

^d This value was confirmed by infrared measurements made by the courtesy of Meyer¹⁷ of the United States Rubber Co.

^e Only two alfin anions were present but the *n*-propoxide seemed to cause about the same effect on 1,4-polymerization as the isopropoxide did, although without equal effectiveness on the yield and viscosity.

^f This sodium chloride was the granular variety and was poorly incorporated in the mixture.

^g Actually three alfin anions were present in this reagent but the lithium cation interfered with the influence which the bromide anion might have had.

^h This catalyst contained a mixture of allylsodium and amylsodium in the ratio of approximately 2 to 1.

than doubled by the presence of certain salts¹¹. In the metalation of *tert*-butylbenzene, the position and amount of metalation is subject to wide variation by the presence of salts which at one time would have been supposed to be inert¹². Some tertiary alkoxides have pronounced effects in dimetalation of the hydrocarbon¹³. In the pyrolysis of amylsodium¹⁴ the percentage and manner of decomposition is subject to this type of control. The effect of polymerization by a sodium reagent is, therefore, quite in line with other behavior. By the choice of proper salts to accompany allylsodium, with proper care in the quantity of catalyst used and with some attention to the details of recovery, a polybutadiene can now be obtained which has a weight average molecular weight¹⁵ of around 7,000,000, the highest known value for any synthetic polybutadiene which is also soluble. Great possibilities in this method of control of the preparation of diene polymer are thus revealed.

TABLE IX

INFLUENCE OF SALTS ON THE POLYMERIZATION OF ISOPRENE BY ALLYLSODIUM AND ON THE UNSATURATION OF THE POLYMERS

Allylsodium and sodium allyloxide with	Yield (%)	Intrinsic viscosity	Gel (%)	Total unsatn. (%)	Ext. bonds (%)
Na isoprop.-NaCl	5	6.3	3	85	11
Na isoprop.-NaSCN	12	8.0	21	89	16
Na isopropoxide	3	3.0	17	69	24

IODINE MONOCHLORIDE TEST FOR ALFIN POLYBUTADIENE

When iodine monochloride was added to a solution of alfin polybutadiene in carbon disulfide-chloroform (60-40) in the determination for total unsaturation⁹, a precipitate, which always occurred and made the results unreliable, proved useful instead as a test for these alfin polybutadienes. Under the specified conditions the precipitate formed within 10 minutes, whereas with polybutadienes prepared by sodium reagents several hours were required. In the presence of ordinary sodium rubber, as little as 0.25 per cent of alfin polybutadiene was thus detected. This test was applied to those products listed in Tables I, II, and III which had low intrinsic viscosities but had been made by reagents whose compositions have produced alfin polymers. In every case a precipitate formed where the proper components in the catalyst had been present and did not form when they were not there. Every mixture which gave a positive test always gave the same test in subsequent experiments.

The success of the test is possibly due to the unusual molecular weight of the alfin polybutadiene. The alfin rubber from a benzylsodium-sodium isopropoxide-sodium chloride catalyst gave a precipitate also, although the average intrinsic viscosity of this polymer is lower than from the better catalyst. Actually alfin polybutadienes of low intrinsic viscosities such as were produced by some of the catalysts tested early in this work¹⁸ may be mixtures of an alfin polymer of very high molecular weight and an ordinary sodium-type polymer of low molecular weight, because with catalysts numbers 7 to 11 in Table I polymers of very low intrinsic viscosities were formed although the precipitation test was positive, indicative of a small amount of alfin polymer present. In this group the only alfin catalyst that was present was the mixture of allyl-sodium, sodium isopropoxide, and sodium chloride that regularly produces polymers with intrinsic viscosities of 10 and above. Also, in Table V, the two forms of polymerization took place simultaneously in numbers 3 and 5 and the polymers could be separated by their comparative solubilities in pentane. The test does not apply to alfin polyisoprene.

EXPERIMENTAL PROCEDURES

General procedures.—All preparations of reagents were carried out in the high-speed stirring apparatus⁷. The speed was at 5000 r.p.m. except in a few cases designated. Where sodium metal had a tendency to agglomerate, the stirring was much slower and is described as cautious. All additions of alcohol or alkyl halide to alkali metal or alkali metal reagent were dropwise and the mixtures were always stirred 30 minutes or longer after addition was completed. The need for care during these steps cannot be overemphasized. No preparation should be attempted unless the apparatus is properly shielded. An attendant should be present at all times in order to control the reaction and particularly to avoid any chance that vibration would loosen a stopcock or otherwise alter the rate of addition. The making and handling of all reagents, their transfer to storage bottles, and the removal of samples for test were done under an atmosphere of dry nitrogen. The general techniques for these steps as well as for the tests on polymerization were the same as have already been described¹⁹. Pentane was usually the medium for all reactions.

Reagents.—Most of the reagents used in this work have been described in previous publications. The *n*-amyl chloride was filtered through calcium chloride, alumina and calcium sulfate (Drierite) as mentioned in a previous paper¹¹.

Allyl alcohol (Eastman Kodak Co., pure grade) was distilled (boiling point 66° to 97° C uncorrected and n_D^{20} 1.4140) before use.

Diallyl ether of 95 per cent purity was obtained through the courtesy of the General Mills Co. research laboratory. It was dried over calcium chloride and then fractionated to remove the binary isotope which contained 30 per cent allyl alcohol and boiled at 89.8° C. The fraction which boiled at 94.8° C was used in the experiments.

Cesium fluoride preparation was from anhydrous hydrofluoric acid and cesium bromide, which was obtained through the kindness of the Dow Chemical Corp.

Lithium iodide (Mallinckrodt's) was powdered by mortar and pestle in a dry box and dried over phosphorous pentoxide for 4 days. It was then recrystallized²⁰ from anhydrous acetone and finally dried at 80° C in a vacuum oven over phosphorous pentoxide.

Sodium hydride was obtained through the courtesy of the Metal Hydrides Co., Beverly, Mass.

Preparation of reagents with granular halide salts and other technically available material.—2-Propanol (6.0 grams of 0.1 mole) was added slowly to 0.1 gram atom of sodium sand and 0.4 mole of dried commercial halide salt or other solid suspended in 400 cc. of pentane with stirring at 8000 r.p.m. Thereafter the mixture was stirred 3 hours before being transferred to a storage bottle. This mixture was added to 0.8 gram atom of sodium and, the whole diluted with pentane to 500 cc. and stirred cautiously, while 0.2 mole of 2-propanol in an equal volume of pentane was added at 10° C. The tendency for the metal to clump was particularly troublesome when potassium fluoride was present. After addition was completed, the temperature was allowed to rise to 20° C while the mixture was stirred at 5000 r.p.m. Diallyl ether (29.4 grams or 0.3 mole) was added over one-half hour while the temperature was maintained at 20° to 25° C. The stirring was continued for 2 more hours before the brown-colored mixture was transferred to a bottle and diluted with pentane to 600 cc. This procedure was the one ordinarily used for the preparation of the reagents used in Tables II and III.

In general the yield of allylsodium, judged by carbonation, was around 60 per cent.

Tests with sodium hydride, sodium hydroxide, and sodium methoxide.—The preparations listed in Table III which contained sodium hydride, sodium hydroxide, and sodium methoxide were made with a slight alteration of the above technique. 2-Propanol (0.2 mole) was added to 0.7 mole of sodium hydride in pentane. The mixture was stirred for 2 more hours before addition to the reaction mixture which was to be used for cleavage of diallyl ether. For the reagent that contained sodium hydroxide, a mixture of 0.1 mole of 2-propanol and 0.4 mole of water was added at 10° C to 0.5 gram atom of sodium while the mixture was stirred cautiously. After evolution of hydrogen had ceased, the suspension was stirred for 2 hours before its introduction into the mixture where cleavage of diallyl ether was to be effected. The same procedure was used for the reagent that contained sodium methoxide except that methanol was used in place of water.

Effect of sodium isopropoxide and sodium halides on the activity of allylsodium.—The reagents for these tests were made in the same way as previously described except that the mixtures of salts were not stirred so thoroughly. The results are listed in Table I. For reagent 1, sodium isopropoxide was made by the addition of 0.1 mole of 2-propanol to 1 gram atom of sodium sand. After

30 minutes more of stirring, 0.15 mole of diallyl ether was added at 20° C. The temperature was then raised to 50° C and held there for 4 hours before transfer to a storage bottle. This material caused no appreciable polymerization of butadiene when 25 cc. were used, whereas 3 to 10 cc. of an alfin reagent usually show high activity. No better result was obtained 2 weeks later. Carbonation of the remainder produced 6.9 grams of vinylacetic acid (61 per cent yield) and 0.7 gram of crotonic acid, the latter presumably by rearrangement from the former.

Similar cleavages of diallyl ether were carried out in the presence of sodium isopropoxide and sodium halides made by Wurtz reactions, *sec*-butyl chloride being used for sodium chloride, ethyl bromide for sodium bromide, and ethyl iodide for sodium iodide. Each alkyl halide (0.2 mole) was added to 1 gram atom of sodium in 500 ml. of hexane at -10° C over 1 hour. After 30 minutes' more stirring, 0.2 mole of 2-propanol was added at 10° C. The temperature was increased to 35° C, and 0.3 mole of diallyl ether was added during 30 minutes. After 2 more hours' stirring, the mixture was transferred to a storage bottle. Reagents 3, 12, and 14 were thus prepared.

For reagent 2, the Wurtz sodium chloride was made by addition of 0.2 mole of amyl chloride to 1.0 gram atom of sodium. Thereafter, 0.2 mole of allyl alcohol was added to destroy the amylsodium and 0.3 mole of diallyl ether was then cleaved.

For the tests where sodium halide was added before and after the cleavage reaction (reagents 4, 5, and 6), the mixture of sodium halide and sodium isopropoxide was made by addition of 0.8 mole of amyl chloride at -10° C to 1 gram atom of sodium during 90 minutes. After stirring for 60 minutes more, 0.2 mole of 2-propanol was added at 10° C, followed by stirring for 90 more minutes. During these reactions the blue color of the amyl-sodium was replaced by a steel gray. The mixture was transferred to a storage bottle. Half of this mixture was added to 1 gram atom of sodium sand to which was then added 0.2 mole of 2-propanol at 10° C, with cautious stirring. Cleavage of 0.35 mole of diallyl ether was effected at 35° C. After being stirred 2 more hours, this mixture was transferred to a storage bottle and used as reagent 4. The other half (300 cc.) was added to a suspension of allylsodium which had been made from 1 gram atom of sodium, 0.2 mole of 2-propanol, and 0.35 mole of diallyl ether and, as reagent 5, had been found inactive. The mixture of three salts was stirred for 5 hours at 5000 r.p.m. before transfer to a storage bottle and, as reagent 6, proved catalytically active.

For reagent 8, the granular sodium chloride, previously ground in the high-speed stirring apparatus, was present during the preparation of the isopropoxide and the subsequent cleavage reaction. The catalyst had a perceptible amount of activity, but a second preparation, number 9, was not equally successful. In reagent 10, the sodium chloride was added prior to making the sodium sand. In reagent 11, the granular sodium chloride was ground for over an hour in decane by high-speed stirring, before addition to the sodium prior to making sand. In reagent 12, the sodium chloride was ground separately, as in reagent 8, except that the stirrer shaft was grounded in order to remove a static charge which caused a troublesome deposit of the finely ground salt on the wall of the glass flask.

Reagents that contained allylpotassium and(or) potassium isopropoxide.—These preparations (for Table V) were carried out in the same manner as the analogous sodium reagents described for Tables II and III except for substitu-

tion of potassium for sodium during the preparation, as indicated. More care must be taken in preparing these reagents because of the highly exothermic character of the reactions. The cleavage of diallyl ether took place at 10° C when potassium metal was used. For reagents 3 and 4, the potassium isopropoxide was prepared separately in an amount approximately equal to the allylsodium to be produced and added to the suspension of amylsodium before admission of propylene.

The polymerizations with the all-potassium reagent were carried out at room temperature behind a safety glass shield. The reactions were very exothermic. If enough reagent were used, the pressure bottle exploded. In no case, however, did any high molecular weight rubber form. At -10° and -30° C no appreciable polymerization took place.

Effect of sodium allyloxiide on the preparation of an alfin catalyst from amylsodium and propylene.—The preparation of an alfin catalyst from 1 gram atom of sodium, 0.5 mole of amyl chloride, 0.35 mole of 2-propanol, and propylene was carried out in the usual way¹⁹, for method B, except that in a series of preparations the 2-propanol was replaced by mixtures of allyl alcohol and 2-propanol. Each catalyst mixture was then tested for its activity toward butadiene, and a portion was also carbonated in order to determine the content of unsaturated carboxylic acid that was expected to be vinylacetic acid. For the control catalyst, where no alcohol was used, the grams of polymer produced for each milliequivalent of unsaturated acid varied from 3.1 to 4.0. As allyl alcohol replaced 2-propanol the activity decreased somewhat, and at a mole ratio of 2.5 isopropyl to 1 allyl alcohol the yield was 1.5 grams. At a ratio of 1.5 to 2.0 the yield was only 0.08 gram, and at 1 to 2.5 and higher, no polymer was produced.

Qualitative examinations of the unsaturated acids obtained by carbonation indicated that the quantity of vinylacetic acid was small and that sodium allyloxiide was being metalated. To demonstrate the susceptibility of this oxide to attack by amylsodium, allyl alcohol (11.6 grams or 0.2 mole) was added at 10° C to a rapidly stirred (4000 r.p.m.) suspension of amylsodium prepared from 1 gram atom of sodium. After being stirred 3 more hours, the mixture was transferred to a bottle and stored for 2 weeks. Carbonation yielded a water-soluble acid which, unlike caproic acid, was not extracted by petroleum ether but was recovered from the ether extract as a red sirupy liquid (7.1 grams). It was soluble in water, ether, or alcohol and was insoluble in pentane or benzene. It decolorized bromine and permanganate. Attempts to isolate a product or derivative of a monocarboxylic acid from allyl alcohol were unsuccessful and the material behaved as the carboxylic acid from a dimeric or higher polymer of allyl alcohol. The crude material had a neutralization equivalent of 204 and a molecular weight of 227. Ultimate analysis was correct for $C_7H_{12}O_4$. Distillation at pressures below 0.1 mm. in a short path still caused the sirup to harden as if the acid were α,β -unsaturated. A repetition of the experiment with the metalated mixture allowed to stand for only 2 hours and with decomposition with ethyl bromide instead of carbon dioxide, yielded material from which 3 grams distilled at 140° C at 1 mm. and which had a molecular weight (Rast) of 245, approximately equal to a trimer.

Effect of sodium allyloxiide on an alfin catalyst.—A stock solution of sodium allyloxiide was made by addition of the amount of allyl alcohol needed to react with the amylsodium that had previously been prepared from 3 gram atoms of sodium and was found to be present in 82 per cent yield, determined by carbonation. The mixture was thoroughly stirred for 1 hour, allowed to stand over-

night, then stirred again for a short period before transfer to a storage bottle where the suspension was diluted to 1500 cc.

An alfin catalyst was made from 3 gram atoms of sodium, 1.5 moles of amyl chloride, 0.35 mole of 2-propanol, and propylene at -10°C in the usual manner. Carbonation showed that each 400 cc. of this suspension contained 44.2 meq. of allylsodium and 3.8 meq. of amylsodium, the presence of the latter being caused by the usual failure of the reaction of amylsodium with propylene to be complete. To 400-cc. aliquots of the catalyst was added enough of the sodium allyloxide suspension to give ratios of 0.525, 1.05, 1.48, and 2.00 for the allyloxide to allylsodium, and the volume of each was diluted with pentane to 550 cc. These four mixtures were designated as A, B, C, and D, respectively. Each mixture was stirred at 5000 r.p.m. for 2 hours in a 1-liter flask as was also a control portion of the catalyst without sodium allyloxide but diluted to 550 cc.

Duplicate tests for catalytic activity of each suspension were made at stated intervals by bottle polymerization with 5 cc. of the catalyst, 30 cc. of butadiene, and 200 cc. of pentane that had been dried over amylsodium. These tests ex-

TABLE X
COMPARATIVE ACTIVITY OF ALFIN CATALYSTS IN THE
PRESENCE OF SODIUM ALLYLOXIDE

Catalyst	Control	A	B	C	D
Yield* (%)					
2 days	41	67	66	70	—
24 days	88	80	85	80	82
47 days	76	55	73	77	76
69 days	78	75	81	73	74
112 days	29	35	61	—	52
Intrinsic viscosity					
2 days	9.9	16.2	11.6	7.4	—
24 days	18.1	21.9	21.9	16.2	15.4
47 days	18.3	19.3	20.9	16.9	20.9
Gel, %					
2 days	57	71	58	46	—
24 days	68	55	74	52	24
47 days	43	51	64	36	53

* Yield of polymer after the catalyst had aged for the number of days indicated.

tended up to 112 days after the catalysts had been prepared. No important difference could be noted in the effectiveness of the reagents (Table X).

After the 112-day test, the activity of each mixture had deteriorated about equally, probably because repeated opening of each bottle to remove samples for testing had permitted some contamination with air. The control actually showed more deterioration than did the four with sodium allyloxide. The two suspensions with larger amounts of sodium allyloxide thickened appreciably, probably because of a small amount of metalation of the sodium allyloxide by the amylsodium that was present and the consequent dimerization or polymerization of that salt, as described before. This change in the physical condition of the catalyst had no influence on polymerization activity other than that caused by the greater difficulty of removing exactly 5 cc. of the catalyst for the test.

Effect of lithium isopropoxide on the catalyst.—In the first series, amylsodium was prepared from 3 gram-atoms of sodium and 1.5 moles of amyl chloride. For the control experiment 0.66 mole of 2-propanol was added. Propylene was then passed into the mixture in the usual way. If the yield of amylsodium

were 82 per cent, and the conversion to propylene quantitative, the quantity of allylsodium would be 0.6 mole. As a rule this yield was reached. The ratio of allylsodium to alkoxide would then be approximately 1:1. To obtain the excess alkoxide listed in Table VI, more alcohol was added. A total of 0.9 mole of 2-propanol or 0.3 mole of 2-propanol with 0.6 mole of *tert*-amyl alcohol was used for the second and third reagent of the table. Where the potassium and lithium alkoxides were added, the salt was first prepared from 0.6 mole of the metal with 1.08 mole of 2-propanol and the alcohol-alkoxide mixture then added to amylsodium prepared from 2.4 gram atoms of sodium and 1.2 moles of amyl chloride. The concentration of amylsodium varied accordingly in these preparations.

In the second series the amylsodium was prepared from 1 gram atom of sodium and 0.5 mole of amyl chloride. To this mixture was added 0.225 mole of 2-propanol with isopropoxide (made by addition of alcohol to the metal) in the amounts given in Table VII.

TABLE XI
PRECIPITATION OF POLYBUTADIENES BY IODINE MONOCHLORIDE

Cat. no.	Inorganic salt ^a	Polymer yield (%)	Intrinsic viscosity	Time for ppt. to appear (min.)
1	None	15	0.8	420
2	NaCl	7	11.3	3
3	NaCl	2	1.4	10
4	NaCl	5	3.2	5
5	NaCl	22	0.8	3
6	NaCl	2	1.2	5
7	NaF	2	1.0	150
8	Na ₂ SO ₄	3	1.8	150
9	LiCl	2	1.1	360
10	KCNO	9	3.1	300
11	LiBr	7	0.6	360
12	NaCl ^b	15	0.4	2

^a Allylsodium and sodium isopropoxide were the other two components of the reagent.

^b The polymer tested was made by a benzylsodium instead of an allylsodium reagent and the catalyst was made by method B instead of C.

Reaction of the polymers with iodine monochloride.—The general procedure was the same as described by Kolthoff and coworkers¹⁸ for the analysis of the number of double bonds. As used for the detection of alfin polybutadienes (made by pouring a benzene solution into 0.2 per cent methanolic phenyl- β -naphthylamine solution) in this study, 40-mg. samples of the dried precipitate were dissolved in 10 cc. of chloroform and 25 cc. of carbon disulfide in 50-cc. volumetric flasks. Ten cc. of a chloroform solution which contained 0.178 gram of iodine monochloride was added to the polymer solution, the contents of the flask were mixed, and the volume was raised to 50 cc. by addition of carbon disulfide. The white flocculent precipitate could be best observed in the deep red solution by looking through the flask into a strong light while gently swirling the contents. Some results with a variety of catalyst preparations are given in Table XI.

SUMMARY

The alfin catalyst is a combination of sodium salts which causes butadiene to polymerize at extreme rapidity in such a fashion that a greater difference exists between sodium and alfin polymerization than between sodium and emulsion polymerization.

Hitherto the combination has been assumed to be binary—allylsodium and sodium isopropoxide—but a new method of preparation has revealed that a halide or pseudohalide salt is essential. Chloride, bromide, and iodide salts of sodium and potassium can be used as the halide component, but fluoride and lithium salts, as a rule, cannot be so employed unless the small size of each ion is compensated by a large cation or anion, respectively, as found in cesium fluoride or lithium iodide. The sodium cation is required for the catalyst. The potassium ion can be tolerated in the alkoxide or halide, but not simultaneously in both. The lithium ion is in general unsuitable. Alfin polybutadiene is differentiated from sodium-polymerized butadiene by a high proportion of 1,4-structure and by an abnormally high intrinsic viscosity. Iodine chloride causes the polymer to precipitate from solution.

All results indicate that polymerization by sodium reagents is in considerable degree controlled by the association of other salts with the sodium reagent.

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STUDIES OF THE VULCANIZATION OF RUBBER. X. THE VULCANIZATION OF NATURAL RUBBER WITH A MIXTURE OF SULFUR DIOXIDE AND HYDROGEN SULFIDE *

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In Parts I-III of this series¹, we developed the hypothesis that the phenomenon of optimum vulcanization, that is, the presence of a minimum or maximum on the kinetic curves of changes of the physical and chemical properties of vulcanizing mixtures, is the result of opposing processes, some of which cause structure formation in the rubber hydrocarbon, while others cause its destruction. The processes of structure formation are caused by the development of local intermolecular bonds as a result of the establishment of active groups of the vulcanizing agent in the molecular chains, as well as by the development of chemical bonds of another type between the chains. The destructive processes consist principally of heat degradation and oxidative degradation of the molecular chains of the rubber.

In conditions where the processes of structure formation prevail throughout vulcanization, a maximum will be observed on the kinetic curves of tensile strength only when the spatial chain of the vulcanizate remains so dense that it impedes the formation of highly oriented, in the border case of crystalline, vulcanized particles during stretching. This same phenomenon was studied in a work of Dogadkin and Karmin², and another of Dogadkin, Bartenev, and Novikova³.

In the opinion of the authors regarding the vulcanization optimum, it is of particular interest to investigate vulcanization under conditions where the destructive processes are absent. In this case one would expect the kinetic curves to become smooth, with neither maximum nor minimum.

A similar case is presented by vulcanization by the Peachey method⁴. This consists of treating rubber with a mixture of sulfur dioxide and hydrogen sulfide at room temperature. In these cases the reaction follows the equation:



and the resulting atomic sulfur can react with rubber at a low temperature. Unquestionably, the course of this reaction is much more complicated, since both reagents: H_2S and SO_2 , can react with rubber in a catalytic reaction, bringing about polymerization and condensation processes⁵. Since, however, according to Peachey, vulcanization takes place at room temperature, then, evidently independent of the mechanism of the reaction, the destructive processes due to the influence of oxygen and high temperature are absent in this process.

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EXPERIMENTAL

In this investigation, films were prepared from Brazilian Hevea latex (jatex type) by pouring it onto carefully washed glass plates.

These specimens were chosen, because, in latex films, rubber retains its properties to the highest degree, and is not subject to destructive processes which are inevitable in the preparation of films from solutions of plasticized rubber. In order to prevent the deformation of the films when they were

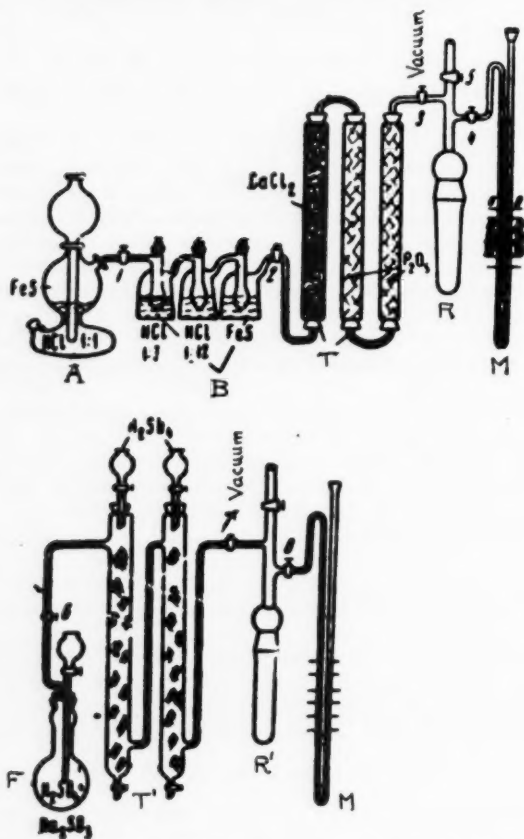


FIG. 1.—Diagrams of vulcanization apparatus and of the sulfur dioxide and hydrogen sulfide generators.

taken off the glass plate, their edges were cemented onto rectangular frames of thick cotton which served as a "carcass" at the moment of removal of the film. The films were then cemented to the four sides of a frame of straight parallelo-piped shape, whose edges were made of glass rods. The frame with the films, dried to a constant weight in a vacuum agitator over calcium chloride, was put in the reactor R of the apparatus depicted in Figure 1. The reactor was

provided with three taps, 3, 4, and 5. At first, taps 3 and 4 were closed, and the reactor was evacuated with an oil pump; then tap 5 was closed, and through tap 3 the reactor was gradually, in 15 minutes, filled with hydrogen sulfide at atmospheric pressure. The pressure was controlled by a manometer M filled with vaseline. Vacuum was created by the absorption of the gas by the films in the reactor; then more hydrogen sulfide was introduced through tap 3. This process was continued until the rubber was completely saturated.

Hydrogen sulfide was prepared in a Kipp apparatus A by the reaction of hydrochloric acid 1:1 on iron sulfide. In order to purify the gas from arsenical compounds, it was passed through washing bottles B containing decreasing concentrations of hydrochloric acid. Then, in order to neutralize the acid, the gas was passed through a water suspension of finely ground iron sulfide, and finally, to eliminate moisture, through tubes T containing calcium chloride and phosphorus pentoxide.

After the films were completely saturated with hydrogen sulfide, they were taken out of the reactor R and immediately put in another reactor R' filled with sulfur dioxide at atmospheric pressure. A second variation of this operation was also used, as will be shown later: first, the films were saturated with sulfur dioxide and then were transferred to a hydrogen sulfide medium. As the sulfur dioxide reacted with the hydrogen sulfide in the films, a partial vacuum was created in the reactor; then tap 7 was closed and more sulfur dioxide was introduced. The films remained in the reactor until the end of the gas reactions, as indicated by the manometer.

The sulfur dioxide was prepared in a flask F, provided with a funnel. Dry sodium sulfate was placed in the flask, and dilute (2:1) sulfuric acid was added dropwise. The resulting gas was passed through drying tubes T', filled with concentrated sulfuric acid. The concentration of sulfur dioxide and hydrogen sulfide was measured by the Reich method.

After vulcanization, the films were placed in a vacuum agitator to evacuate inert gases and moisture. This process was continued until the films reached a constant weight.

Inasmuch as literature on the solubility of sulfur dioxide and hydrogen sulfide gives data only for smoked sheet rubber, we considered it necessary to determine the solubility of sulfur dioxide in latex films. Therefore we placed a quartz spring balance in reactor R', controlled in this case thermostatically at 20°C , and measured the weight increase of a film in an atmosphere of sulfur dioxide at a pressure of 760 mm. mercury.

We established that the solubility of sulfur dioxide in latex films at 20°C and 760 mm. mercury is 2.54 per cent, which represents a coefficient of absorption of 7930 cc. per liter. The coefficient of absorption of hydrogen sulfide is 970 cc. per liter. The equilibrant concentration in films of thickness up to 1 mm. is reached within 30–40 minutes.

It was also extremely important to determine whether the hydrogen sulfide and sulfur dioxide react independently on the latex film, since the additional weight of the film after vulcanization is attributed principally to the sulfur formed in the reaction of the gases. Two previously weighed specimens were taken, one of which remained 5 hours in an atmosphere of sulfur dioxide, and the other in hydrogen sulfide. At the end of this period the specimens were evacuated and agitated in a vacuum for 2 hours.

Table 1 shows the results of these experiments:

TABLE 1
ABSORPTION OF HYDROGEN SULFIDE AND SULFUR DIOXIDE
BY LATEX FILMS

Conditions	Saturation of SO ₂	Saturation of H ₂ S
Weight of specimen before saturation	0.3333	0.7800
Weight of specimen after saturation	0.3425	0.7823
Weight of specimen after 20 minutes in air	0.3400	0.7800
Weight of specimen after evacuation for 2 hours	0.3334	0.7800

In neither case did the shape or elasticity of the films change as a result of the action of the gases.

Table 1 shows that the absorption of sulfur dioxide and hydrogen sulfide by latex films is a temporary process, and that, under these experimental conditions, there is no chemical reaction between the rubber and either of the two individual gases. On the basis of this, it is possible to observe the kinetics of vulcanization by measuring the increase in weight of a film, as was mentioned at the beginning of this work.

Changes of the physical and chemical properties of vulcanizates were measured: (1) by the amount of bound sulfur measured by the Henriksen method; (2) by the amount of acetone extract (including free sulfur), measured by the bromine method; (3) by the swelling maximum in acid, determined in a Dogadkin apparatus⁶ at 20° C, and (4) by the tensile strength and elongation at rupture and residual elongation, measured on a Polyani dynamometer at a rate of stretching of 8.5 mm. per minute.

KINETICS OF VULCANIZATION

In the study of the kinetics of vulcanization, films dried in a vacuum agitator were first saturated with sulfur dioxide, which has a high absorption coefficient, and then were transferred to a reactor with hydrogen sulfide, where they were exposed to constant gas pressure. The time that the specimen remained in hydrogen sulfide was equal to the time of vulcanization; in the extreme case it reached 120 minutes. After the necessary period in hydrogen sulfide, the specimens were evacuated to a constant weight, and the difference was cal-

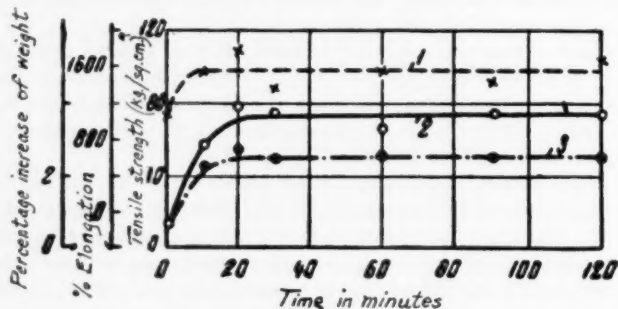


FIG. 2.—Kinetics of vulcanization. 1. Elongation at rupture. 2. Tensile strength. 3. Increase of weight.

culated to be the gain of weight of the specimen, representing the quantity of byproducts of the reaction present in the vulcanizate. The results of the experiment are depicted in Figure 2. We see that the kinetic curves of change of tensile strength and elongation at rupture have no maximum or minimum. They are functions of the smooth curve of kinetics of the chemical reaction.

Thus, under these conditions, as a result of the absence of destructive processes, the phenomenon of a vulcanization optimum is not observed. Since the change of mechanical properties is due only to the constructive action of the reacting ingredients, the dynamics of this change is expressed by smooth curves without either maximum or minimum. In other words, these results agree perfectly with our theory of the phenomenon of vulcanization optimum.

RELATION OF THE PROPERTIES OF A VULCANIZATE TO ITS SULFUR CONTENT

The slight solubility of sulfur dioxide in rubber prevents a sufficiently thorough degree of vulcanization. The highest concentration of sulfur in this vulcanizate did not exceed 2.5 per cent. In order to assure a greater degree of

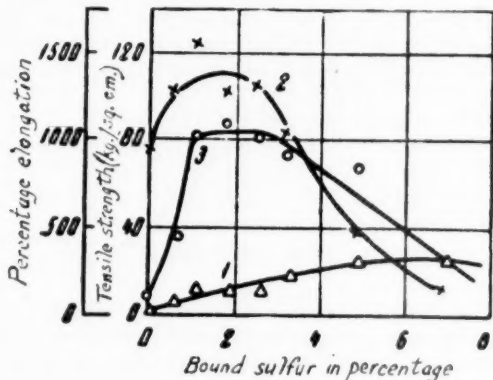


Fig. 3.—Changes of properties of vulcanizates with change of sulfur content. 1. Modulus. 2. Elongation at rupture. 3. Tensile strength.

vulcanization, the films were treated several times with sulfur dioxide and hydrogen sulfide successively. The results of these experiments are presented in Table 2. We see that not all the sulfur is combined in the vulcanizate; part of it remains free and can be extracted with acetone. The proportion of bound sulfur to the total amount of sulfur increases with increase of the degree of vulcanization.

In this connection, one observes that the total amount of analytically measured free and bound sulfur is somewhat less than the weight increase of the films. This indicates that not only sulfur, but also the other elements of the reacting gases, are incorporated in the film of vulcanizate; in other words, when hydrogen sulfide and sulfur dioxide react simultaneously, they are absorbed. However, the excess of weight increase of the film over the total amount of sulfur is almost equal to the corrected acetone extract. Hence one may assume that, in the same vulcanized rubber, the total and bound sulfur content are equal to the values determined analytically.

TABLE 2
PROPERTIES OF VULCANIZATES PREPARED BY MULTIPLE CYCLES OF
TREATMENT WITH SULFUR DIOXIDE AND HYDROGEN SULFIDE

Number of specimen	Number of cycles and order of saturation	Excess weight of sulfur (%)	Total sulfur (%)	Free sulfur (%)	Bound sulfur (%)	Acetone extract (%) ^a	Bound sulfur / Total sulfur
1	One, beginning with H ₂ S	1.59	0.96	0.35	0.61	4.31	0.63
2	Two, beginning with H ₂ S	2.26	1.61	0.51	1.10	4.10	0.68
3	One, beginning with SO ₂ , and one beginning with H ₂ S	3.64	2.63	0.76	1.87	4.48	0.71
4	Two beginning with SO ₂	4.36	3.63	1.03	2.60	4.32	0.72
5	Two beginning with SO ₂ , and two beginning with H ₂ S	5.0	3.89	0.70	3.19	4.86	0.80
6	Two beginning with SO ₂ and two beginning with H ₂ S	7.0	6.00	1.65	4.83	4.21	0.80
7	Three beginning with SO ₂	9.60	8.61	1.82	6.79	3.86	0.80
	Unvulcanized film	—	0.039	0.027	0.01	3.51	—

^a In this column is given the corrected acetone extract, subtracting the sulfur analytically determined in it.

Figure 3 gives the changes of the physical and mechanical properties of a vulcanizate in relation to the bound sulfur content. We see that the modulus increases progressively, and the swelling maximum of the vulcanizate decreases progressively with increase of bound sulfur content. Such a change of these values, in agreement with contemporary theories⁷ is a direct index of the increase of the number of cross-links between the chains.

From the swelling maximum according to Flory's formula:

$$\ln \left(1 + \frac{1}{Q_m} \right) (Q_m + 1)^{-1} = \mu (Q_m + 1)^{-2} + \frac{\rho V_0}{M_c} (Q_m + 1)^{\frac{1}{2}}$$

where Q_m is the swelling maximum, expressed as $Q = \frac{V_{\text{swelling}}}{V_0}$; V_0 is the

molecular volume of the solvent; M_c is the molecular weight of a chain segment between the cross-linkages; μ is the coefficient for rubber equal to 0.4; ρ is the density of rubber, was calculated the mean molecular weight M_c , and then the number N of molecules (that is, the number of chain segments between the cross-linkages) per cc. Then, using the equation: $N = 2n + 2$, where n is the number of cross-linkages per cc. of vulcanizate, the amount of bridge sulfur S_M was calculated for each stage of vulcanization, assuming that each bridge contains one sulfur atom. The proportion of bridge sulfur to the total amount

TABLE 3
DENSITY OF SPATIAL NETWORK OF VULCANIZATE FROM SWELLING DATA

Bound sulfur S.B	Swelling maximum Q_m	Molecular weight M_c	Number of chains in 1 cc. $N \times 10^{19}$	Number of nodes in 1 cc. $N \times 10^{19}$	Bridge sulfur S_M in %	Bridge coefficient γ
0.61	7.98	33522	1.65	0.82	0.05	0.079
1.10	6.13	20768	2.67	1.33	0.08	0.070
1.87	4.83	13795	4.01	2.01	0.11	0.062
2.60	4.63	12475	4.83	2.41	0.14	0.054
3.19	3.32	6853	8.79	4.39	0.26	0.080
4.83	2.93	5538	10.97	8.79	0.34	0.066
6.79	2.46	4349	13.94	6.97	0.41	0.060

of bound sulfur was determined as the bridge coefficient γ . The values calculated by this method are shown in Table 3. Figure 4 shows the ratio of the number of cross-linkages to the total amount of bound sulfur in the vulcanizate; we may consider approximately that the number of cross-linkages increases linearly with an increase of sulfur content. Meanwhile, the strength of the vulcanizate, having reached a maximum at a sulfur content of ≈ 3 per cent, which is equal to 7.8×10^{-3} of the bridge formation equivalent of sulfur, then commences to decrease, although no signs of any destructive processes, for example, change of modulus or swelling maximum, are observed. From this one concludes that this decrease of tensile strength, as we showed earlier², is the result of the formation of such a dense network in the vulcanizate that, during deformation, the orientation of the molecular chains is retarded and, consequently, the size of the crystalline phase in the ruptured specimen decreases.

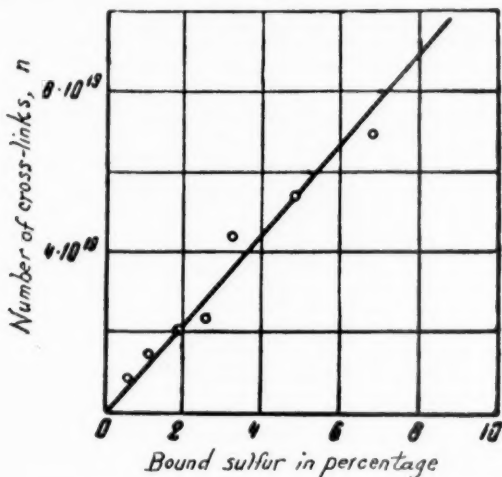


FIG. 4.—Number of cross-linkages of a vulcanizate in relation to its sulfur content.

It is well to remember that the decrease of tensile strength characterizes a vulcanizate in which the segments between the cross-linkages consist of 100–200 isopentene groups ($M_c \approx 7000$), that is, of length approximately 500–1000 Å, on an order surpassing the size of a segment characterizing the heat motion of the molecular chains of the rubber.

As has already been mentioned, a further decrease of these segments obstructs the orientation phenomena during deformation of the vulcanizates. Undoubtedly, the optimum size of the segments between the cross-linkages of the vulcanizates depends also on the type and concentration of the sulfur-bearing intermolecular rings formed during vulcanization, since they have a strong influence on the flexibility of the chains.

CONCLUSIONS

1. The dynamics of the changes of the properties of rubber during vulcanization by a mixture of sulfur dioxide and hydrogen sulfide, in distinction from

conventional vulcanization by sulfur, is expressed by smooth curves. No vulcanization optimum is observed.

2. With multiple cycles of vulcanization, the increase of bound sulfur content above 3 per cent results in a decrease of tensile strength.

3. Changes of tensile strength of the vulcanizate dependent on changes of sulfur content are attributable to the influence of the density of the spatial network on the orientation processes during deformation.

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POLYMERIZATION AND COPOLYMERIZATION REACTIONS WITH ALFIN CATALYSTS

IN RELATION TO MASTERBATCH PREPARATION *

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Polymerization of monomers by alfin catalysts¹ has been reported as being unusual both with regard to conversion of monomer to polymer² and resulting polymer characteristics³. Physical tests have shown that the properties of polybutadiene prepared from certain alfin catalysts were superior to those of polymers produced in emulsion. The properties of butadiene-styrene copolymers prepared similarly were at least comparable to the properties of emulsion copolymers. These characteristics may be of value in producing polymers which yield vulcanized stocks with good hysteresis characteristics or improved physical properties at high temperatures. The very high intrinsic viscosities reported⁴ suggested the possibility of extending the oil-masterbatch type of polymer to even higher concentrations of oil than those used with high viscosity cold rubber under active study in 1949 and 1950. Some experiments of this type appear to have been done⁵.

EXPERIMENTAL

PREPARATION OF CATALYST AND POLYMERIZATION PROCEDURE

The method of preparation of the catalyst was that used by Morton⁶. It has been found possible to replace the 99 per cent pure *n*-pentane with technical grade material (95 per cent purity) and to substitute a refinery cracked C₃ cut for the pure propylene without loss of catalyst efficiency. The catalyst was tested by its ability to polymerize butadiene. Eight-ounce screw-cap peroxide bottles fitted with Koroseal and Butyl gaskets were used. Ingredients consisted of 75 grams of *n*-pentane, 10 grams of butadiene (approximately 97.5 per cent), and catalyst. In general, the charging procedure was *n*-pentane, butadiene, and catalyst injected by syringe and needle. In the few other cases, the pentane, catalyst, and then butadiene were charged, and the bottle was immediately capped. No difference in the rate or degree of reaction was observed between the two methods. The bottles were shaken to disperse the catalyst and let stand at room temperature until completion of reaction (at least 2 hours). Phenyl- β -naphthylamine, 1.5 parts on the monomer charged, was then added as a 0.75 per cent solution in methanol. The methanol destroyed any remaining catalyst, while the phenyl- β -naphthylamine served as antioxidant. The polymers were removed from the bottles and washed thoroughly with water to remove sodium hydroxide, sodium chloride, and *n*-pentane. Washing of the polymer was difficult because of its swollen nature,

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and some sodium chloride probably remained in the polymers. Conversion was determined by drying in a vacuum desiccator, with continuous pumping at room temperature. Conversion results tended to be high because of residual nonrubber materials. If these polymers were extracted by ethyl alcohol-toluene azeotrope and dried, the resulting yield fell below a calculated value of 100 per cent. Most of the studies were done using unextracted polymers, so the true conversions are somewhat lower than those reported. The results should not be invalidated since conclusions are drawn only when a considerable change in conversion was noted.

The efficiency of batches of catalyst prepared identically varied in that different quantities were required to polymerize the same quantity of butadiene to the same conversion. An arbitrary classification of catalysts as good, fair, poor, and of no value has been set up; of 21 early consecutive batches, the number in each category was 5, 8, 6, and 2, respectively. The catalysts of the respective classes could polymerize over 50, between 34 and 50, between 20 and 34, and no moles of butadiene per mole of "active" ingredient in the catalyst. The active ingredient was considered allyl sodium and was calculated on the basis of an 80 per cent yield of amyl sodium and complete reaction of the amyl sodium with 2-propanol and propylene. Thus in the 1-liter batch 0.2 mole of sodium isopropoxide and 0.2 mole of allyl sodium, or 0.2 mole of active ingredient, were produced. The quantity of active ingredient used in any test bottle was determined either on a volume of suspension or weight percentage basis. Considering the likelihood of molecular weights of the order of 10,000,000 the catalyst had a very low over-all efficiency. The efficiency achieved was comparable to that achieved by Morton⁷ in his earlier experiments. (Subsequent work has shown that the yield of amyl sodium from the amyl chloride available was only about 50 per cent. Thus the actual efficiencies were 5 to 10 times greater than calculated per mole of allyl sodium. Rigorous purification of all ingredients would undoubtedly improve this efficiency but would not yield data of practical importance.)

The efficiency of the catalyst was not highest immediately after preparation. A period of at least 3 days between preparation and use was suggested⁷. Typical increases in catalyst efficiencies for two different catalysts tested after several time periods were obtained. For the first the efficiency increased considerably as the rest period changed from 30 minutes (40 moles of butadiene per mole of allyl sodium) to 5 days (70 moles of butadiene per mole of allyl sodium), with no appreciable decrease after standing as long as 5 weeks. Even after standing 18 hours, the efficiency of the second catalyst was quite low (25 moles of butadiene per mole of allyl sodium) and did not increase with catalyst concentration as shown by the three tests, although the efficiency was good after 6 days (66 moles of butadiene per mole of allyl sodium). This lack of an increase in efficiency is to be compared with tests made after 5 days with the first catalyst, which had achieved its optimal activity and which showed a distinct increase in efficiency with catalyst concentration and conversion. The effect was found to be quite general for catalysts which have stood long enough to achieve their highest efficiencies.

The differences in efficiency of batches of catalyst is believed to result primarily from differences in the sodium sand. While no measurements of particle size are available, poor efficiency may result when the particle size of the sodium sand was larger than usual, resulting in a less satisfactory reaction with amyl chloride. This larger size of the sodium sand may be caused by a slower rate or stirring during preparation.

In certain cases conversion was below normal or reaction did not take place at all. The effect of various materials which might act as poisons was investigated. While it was known that water and alcohols in large quantities destroy the catalyst, it was not known in what concentrations they would be tolerated. To the standard charge of 10 grams of 97.5 per cent butadiene, 75 grams of *n*-pentane, and catalysts the possible poisons were added in various quantities.

Water, 1 per cent based on the monomer, reduced the effectiveness of the catalyst, while 2 per cent concentration not only destroyed the catalyst but produced an inhibitor which prevented reactions even when a large excess of

TABLE I
POLYMERIZATION OF BUTADIENE

Reaction time (min.)	Conversion (%)	$[\eta]$	Gel (%)	$[\eta]$ Corrected
Series A				
2	5	11.2	39	17.7
7	20	9.8	32	10.9
15	40	10.9	14	11.4
40	78	13.6	41	14.1
90	100	8.2	62	8.6
420	97	6.1	71	6.3
Series B				
2	4	—	—	—
7	19	—	—	—
15	21	—	—	—
40	30	—	—	—
90	45	—	—	—
420	47	—	—	—
Series C				
3	13	—	—	—
10	26	—	—	—
20	38	—	—	—
45	42	—	—	—
90	38	—	—	—
Series D				
4	5	10.1	43	17.0
10	10	6.8	23	8.2
25	26	—	—	—
60	81	12.0	26	12.3
110	98	10.4	32	10.6
1140	100	9.9	44	10.1

catalyst was used. Acetone appeared to react similarly, 1 per cent resulting in inhibition. Although methanol reduced catalyst efficiency, it did not seem to cause inhibition at a concentration of 1 per cent. Glacial acetic acid decreased the efficiency of the catalyst markedly with no inhibition at a concentration as high as 2 per cent. Sodium hydroxide added as solid pellets caused no decrease in efficiency of the catalyst. The good conversion when 50 per cent sodium hydroxide solution was added indicated that it might even counteract the effect of water.

The necessity of drying the butadiene currently used in emulsion systems was avoided, since the conversion was not affected. Also polymerization of

butadiene was satisfactory whether the diluent was *n*-pentane, petroleum naphtha, or a mixture of C_4 hydrocarbons or other hydrocarbons.

REACTION CHARACTERISTICS

Polymerization of butadiene and butadiene-styrene mixtures is very rapid, apparently being complete within about 2 hours. Also, Morton⁷ has reported that the polymerization of butadiene by a catalyst similar to the one used resulted in an approximately first-order reaction. It was considered worthwhile to study these systems not only to determine rates of reaction but to study any variations in intrinsic viscosity and gel which might occur as polymerization proceeded.

Table I includes the data for the time-conversion studies of the polymerization of butadiene. Different catalysts were used for the four different series as shown, the same volume of catalyst being used for each bottle in any series. Reaction was interrupted by the addition of 10 cc. of methanol containing 0.15 gram of phenyl- β -naphthylamine. In series A and B solid potassium hydroxide of a concentration of 1 per cent on the monomer was added to the bottles before polymerization with no apparent effect on the reaction.

To determine whether rate of reaction depended on catalyst concentration, sufficient catalyst to cause 100 per cent conversion was added in series A and D, while in series B and C only sufficient catalyst to effect partial conversion of monomer to polymer was used. Series D tended to have a slightly slower rate at low conversions than at higher conversions, while in series C the reaction began rapidly and then appeared to change sharply, becoming slower and then proceeding uniformly until the maximum conversion of approximately 47 per cent was reached.

The addition of methanol at any time should completely destroy the catalyst, and the antioxidant, added at the same time, should stabilize the polymer so that the material recovered after any degree of conversion could be used to measure the intrinsic viscosities and gel contents as a function of conversion. The high intrinsic viscosity (above 10) coupled with a high gel content (40 per cent) for conversions of 5 per cent is to be noted. The decrease of intrinsic viscosity was followed by an increase to a maximal value at a conversion between 40 and 60 per cent. At higher conversions the intrinsic viscosity decreased rapidly until reaction was complete, then more slowly as the polymer remained in the system before stopping. Gel decreased perceptibly until a conversion of 10 to 20 per cent was reached, after which it increased rapidly until reaction was complete; it decreases more slowly as the mass sits. The intrinsic viscosity corrected for the antioxidant present in the polymer, assuming that the phenyl- β -naphthylamine acted only as a diluent, is in the last column of Table I. While the initial value is much higher, indeed the highest value obtained, the same maxima and minima occur at the same conversions. Similarly the gel contents are shifted to higher values at low conversions without any change in the general shape of the curve when corrected for phenyl- β -naphthylamine present. The samples from series A remained in the laboratory at room temperature and were exposed to the general light and air for a period of one month before samples were taken for intrinsic viscosity and gel determinations. The samples from series D underwent similar treatment for a period of one week. Differences between series A and D may indicate that the antioxidant is not functioning effectively.

The high initial intrinsic viscosity indicates that polymerization begins with production of a few very large molecules. The high initial gel indicates cross-linking of the polymer, presumably by metalation or removal of an α -hydrogen, which effect is brought about by the relatively high catalyst concentration. The gel resulting from low conversion tended to be hard, flaky, and tightly bound, while that at higher conversion was a highly swollen material. This effect also would be expected from change in catalyst concentration with conversion.

The characteristics of a butadiene-styrene copolymer differ from those of polybutadiene in many respects. The data for a series charged as a 70/30 ratio of butadiene to styrene are shown in Table II and indicate a reaction essentially identical to that for butadiene with a very fast initial rate which decreased sharply at high conversions. The percentage gel was less in the copolymer than in the pure butadiene polymer. It decreased with conversion until a 75 per cent conversion was reached and then increased somewhat. The intrinsic viscosity increased gradually until reaction was essentially complete and then decreased as the polymer mass was allowed to stand in the presence of the catalyst. These two effects decidedly differ from the butadiene polymer and together produce desirable polymer characteristics—notably, low gel content and high intrinsic viscosity at high conversion.

TABLE II
DATA ON COPOLYMERIZATION OF BUTADIENE AND STYRENE

Reaction time (min.)	Conversion (%)	[η]	Gel (%)	Bound styrene (%)	
				Unextracted	Extracted
4	6	2.5	29	35	26
10	24	6.1	21	30	25
25	57	11.4	14	31	25
60	76	12.6	6	31	27
110	94	13.2	9	29	26
1140	107	9.4	9	30	26

From the results shown for the two systems, it would appear that polybutadiene molecules grow almost instantaneously, an increase in conversion resulting from more molecules being produced, while in the copolymer system styrene slows down the growth so that at low conversions intermediate sized molecules are isolated. If this is true, then the essentially identical rates of conversion would necessitate a faster rate of initiation in the copolymer system than in the butadiene system.

It has been suggested⁸ that, in the alfin system, styrene tends to enter a copolymer with butadiene faster than butadiene. This has been confirmed by these studies. Values of bound styrene on the dried unextracted samples shown in Table II were thought possibly in error, especially at low conversions, as a result of the high concentration of phenyl- β -naphthylamine, which would tend to raise the refractive index and hence the bound styrene value. Because of this, the brownish colored samples were extracted for 30 minutes with the standard ethyl alcohol-toluene extract and washed with acetone and dried, producing white polymers with sharp refractive index lines. The lower results in the column under "extracted" indicates that phenyl- β -naphthylamine or some other material had affected the values, making them too high. Of more importance than this is the constancy of the values, within experimental error,

below the concentration of styrene charged. The absolute values are probably higher than indicated, since a calibration chart for emulsion copolymers was used, which reportedly⁸ gives low values. Thus while indications from this experiment are that styrene enters the polymer at least no faster than butadiene, differences due to incorrect calibration of the method may change this. Evidence to be presented in the next section indicates that styrene does enter the chain slightly more rapidly than butadiene on the average.

Dilution of butadiene has more effect on polymerization characteristics than on properties of the polymer. Increase in dilution, whether the diluent was *n*-pentane or other light hydrocarbons, or a plasticizer, generally decreased the rate of polymerization. Figure 1 shows the percentage conversion plotted against catalyst used for different dilutions of butadiene by *n*-pentane where a constant weight (10 grams) of butadiene was used throughout. For each concentration there is a minimum quantity of catalyst below which amount no polymerization occurred and above which conversion increased rapidly with

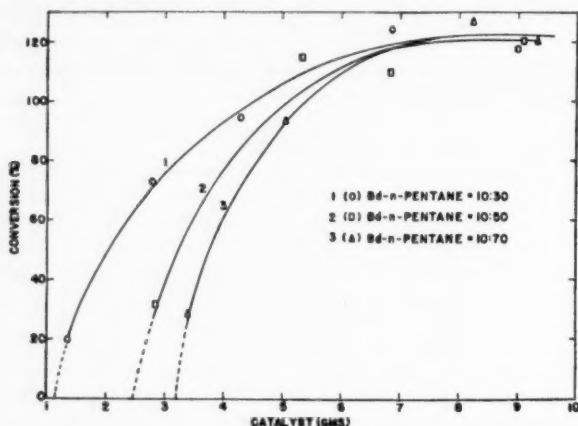


FIG. 1.—Effect of ratio of butadiene to *n*-pentane on conversion achieved with increasing amounts of catalyst suspension.

catalyst concentration. This minimum catalyst requirement decreased with increasing monomer concentration, while the catalyst required for 100 per cent conversion remained relatively independent of concentration. There was a slight decrease of intrinsic viscosity and relatively constant gel content with increasing dilution.

Polymerization of butadiene has been carried out over a temperature range -60° to 40° C. The reaction times were only estimated, but did show a definite decrease of the rate of reaction with decrease in temperature. Associated with this decrease of rate was a very pronounced increase in the density of the polymer. The resulting hard tough polymer did not swell in the pentane, even when the temperature was raised. No decrease of degree of polymerization was noted except at -60° C, where conversion decreased to 77 per cent, and even this decrease might be a result of the lower catalyst content. The decrease in intrinsic viscosity with temperature was fairly regular, *i.e.*, from 14.5 at 40° to 8.1 at -60° C. This effect and the decrease of gel content might be expected

TABLE III
COPOLYMERIZATION OF VARIOUS RATIOS OF BUTADIENE AND STYRENE

Monomers (% styrene)	$[\eta]$	Gel (%)	Polymer (% styrene)
0	20.3	1	0
20	16.9	11	18
40	10.6	5	36
60	9.4	30	50

from a slower reaction, with resulting less complex chain growth, less branching and cross-linking, and less growth before termination.

In the copolymerization of butadiene and styrene, an increase of the relative proportion of styrene resulted in a decrease of the rate of polymerization and increase of fluidity and stickiness of the swollen mass. Also there was a distinct decrease of the nerve and elasticity of the dried polymer with increasing styrene content. The constant conversions of the copolymers in Table III indicate that styrene and butadiene copolymerize completely regardless of charge ratio. The refractive index method of determining bound styrene showed that the values decreased slightly below the quantities charged. The decrease of

TABLE IV
BOUND STYRENE ANALYSIS OF COPOLYMERS

Conversion (%)	Circosol-2XH (pt./100 pts. monomers)	Styrene (%)		Styrene bound (%)/styrene charged (%)
		Charged	Bound	
60	0	20.0	26	1.27
61	0	30.0	36	1.21
80	0	30.0	34	1.15
81	0	30.0	36	1.19
85	0	10.6	13	1.25
100	0	30.0	32	1.07
100	0	40.0	36	0.90
100	0	30.0	30	1.00
100	0	20.0	18	0.90
100	0	60.0	50	0.83
100	0	20.0	19	0.97
100	0	10.5	10	0.98
Oil added after polymerization				
52	96	10.0	12	1.22
81	80	30.0	10	1.00
95	65	30.0	28	0.94
100	65	20.0	21	1.03
Oil added before polymerization				
12	80	30.0	15	0.50
29	65	20.0	5	0.25
38	65	20.0	7	0.36
40	97.2	29.2	14	0.47
57	80	30.0	13	0.44
63	65	20.0	9	0.47
67	110	33.0	21	0.62
68	65	30.0	15	0.51
69	80	10.0	3	0.34
74	80	30.0	15	0.49
80	100	49.7	33	0.66

intrinsic viscosity with bound styrene is linear. The possibly incorrect bound styrene values will result in an incorrect slope of the line.

Bound styrene values for a large number of copolymers produced were determined and are listed in Table IV. In cases where no plasticizer was present in the polymerization mixture, conversions were determined by drying. Where oil was present ethyl alcohol-toluene azeotrope extractions were carried out, conversions determined from the residue, and bound styrene values measured on the dried extracted materials.

The results for polymers prepared in the absence of Circosol-2XH are in the first part of Table IV. Since the ratio of styrene to butadiene charged is variable, it was considered of more value to compare the ratios of bound styrene to that charged as in the last column. Although data below 60 per cent conversion are lacking, the data from 60 to 100 per cent conversion would indicate that the styrene was entering the polymer slightly faster than butadiene initially.

Except for four of these polymers, values of bound styrene were determined for the product resulting from drying. The other four, which had Circosol-2XH added to them after reaction while still in the swollen state, were extracted and bound styrene values were determined on the extracted material. Circosol-2XH has a refractive index corresponding to a butadiene-styrene copolymer containing 5 per cent styrene. Thus a small amount of this material left after

TABLE V
PERCENTAGE INCREASE IN CATALYST REQUIREMENT

Conversion (%)	Increase (%) for system		
	Butadiene plus 80 pts. oil	Butadiene-sty- rene (70/30)	Butadiene-sty- rene (70/30) and 80 pts. oil
60	9.0	10.9	42.7
70	12.8	11.4	46.3
80	18.4	12.8	50.8
90	25.5	15.1	55.4
100	33.6	18.7	61.0

extraction should not affect the correct value appreciably whether the material was of a low or high styrene content.

When polymerization took place in the presence of Circosol-2XH a decided decrease of the bound styrene was noted, as shown in the second part of Table IV. From the scattered data, little indication of a trend may be observed, although the ratio of bound styrene to that charged must be 1 at 100 per cent conversion. The ratio of bound to charged styrene was, in general, not higher than 0.5, compared to at least 1.0 where no plasticizer was present. This indicates that some definite change in the system has taken place as a result of the presence of the plasticizer, perhaps a heterogeneous distribution of monomers.

The copolymerization of styrene with butadiene increased the catalyst requirement, as did the incorporation of a plasticizer oil such as Circosol-2XH. The results of conversions *vs.* catalyst requirement for the systems studied are given in Table V. As the catalyst concentration increased, the increase of conversion was very rapid for butadiene, less rapid for the butadiene-styrene system, and much slower when Circosol-2XH was present. Of particular interest was the fact that the addition of Circosol-2XH to the butadiene-styrene comonomer mixture resulted in a catalyst requirement greater than that expected from adding the separate effects of oil and styrene.

When α -methylstyrene was copolymerized with butadiene, an upper limit to the amount which would polymerize was reached at about 25 per cent, as shown in Table VI. Up to a certain level, the α -methylstyrene seemed to polymerize rapidly, while above this level a rather small increase of bound monomer resulted, even when it was charged in large proportions. As for styrene, the bound α -methylstyrene values have been taken from a calibration chart for an emulsion copolymer and conceivably would suffer the same errors. The intrinsic viscosity was depressed further by a given amount of α -methylstyrene than it was by the same amount of styrene, although some of this effect might result from the lower conversions.

TABLE VI
COPOLYMERIZATION OF BUTADIENE AND α -METHYLSTYRENE

α -Methylstyrene (monomers) (%)	Conversion (%)	$[\eta]$	Gel (%)	α -Methylstyrene (polymer) (%)
0	100	20.3	1	0
18.4	91	14.5	18	13
40.0	62	10.4	7	19
54.6	55	11.6	4	21

In the hope of producing a copolymer of butadiene and isobutylene, bottles were charged in the standard manner with isobutylene in various monomer concentrations, as shown in Table VII. As the charge ratio of isobutylene to butadiene increased, the conversion and intrinsic viscosity decreased. Conversions indicated that at least some of the second monomer was entering the polymer, and the decrease in intrinsic viscosity added weight to this. Total unsaturation of the polymer was determined by the iodine monochloride method^a with slight modifications. The polymers were purified by dissolving in benzene, filtering, and reprecipitating in ethyl alcohol. Solution was achieved by allowing the dried polymer to stand 1 to 2 days in contact with chloroform.

TABLE VII
ATTEMPTED COPOLYMERIZATION OF BUTADIENE AND ISOBUTYLENE

Isobutylene Charged (%)	Conversion (%)	$[\eta]$	Gel (%)	Unsaturation (%)
0	100	19.8	6	91
20	93	17.1	7	88
40	68	17.2	13	92
60	44	13.9	9	94
80	28	13.7	4	94
0 ^a	—	—	—	97

^a Polybutadiene produced in emulsion.

This procedure resulted in a constant blank, regardless of the time of contact of iodine monochloride and polymer solution. Polybutadiene prepared by an emulsion process was used to check the method and showed it to be satisfactory within the limits of experimental error. The lower unsaturation of the alfin polymers, even polybutadiene, indicated that more of the double bonds were not titratable. From the unsaturation evidence no isobutylene entered the butadiene polymer, the decrease of intrinsic viscosity probably resulting from the isobutylene acting only as a chain-terminating agent.

Many of the polymers showed "gel" by the usual methods of analysis. This was very loose and tended to disappear on milling the polymer, on using more

TABLE VIII
CROSS-LINKING OF POLYBUTADIENE WITH DIVINYLBENZENE (DVB)

DVB (pt./100 pts. monomer)	Gel (%)	Swelling index of gel	$[\eta]$
0.00	43	86	11.0
0.00	51	57	14.4
0.10	57	72	7.5
0.20	72	112	6.5
0.50	77	47	3.5
0.80	79	68	6.4
1.10	76	80	6.2

solvent, and on allowing to stand in contact with a solvent for a long time. It was of interest to try to obtain cross-linked polybutadiene of controlled structure.

Cross-linking of butadiene both with divinylbenzene and vinyl crotonate was attempted. Divinylbenzene was added as a 20 per cent solution diluted with inert hydrocarbons; the vinyl crotonate supplied as a 95 per cent solution was diluted to a 10 per cent solution with petroleum naphtha. Swelling index was determined as described¹⁰ with slight modifications. The cage was hung from the top of the bottle instead of resting on a stand. The sample size was decreased to 0.03 to 0.04 gram and 100 cc. of benzene was added, since a more concentrated solution resulted in a solution so viscous that it drained from the cage very slowly. Solution was allowed to proceed for 4 days, whereupon gel was determined by drying. The gel values may be in error because of the slow rate of solution of these polymers and because of the rapid formation of loose gel on allowing the polymers to stand before dissolving. However the results should be relative.

For divinylbenzene the results are given in Table VIII. Gel increased with the concentration of cross-linking agent, apparently leveling off below 80 per cent. This was accompanied by a decrease of intrinsic viscosity of the soluble portion. Since a slight excess of catalyst was used throughout, conversion was essentially complete. The erratic behavior of the swelling index made it impossible to draw any conclusions from it except that the gel did not become appreciably tighter. Of interest is the fact that with an increase of gel, the intrinsic viscosity of the soluble portion decreased, presumably because of removal of the larger molecules by cross linking and subsequent concentration of

TABLE IX
CROSS-LINKING WITH VINYL CROTONATE

Vinyl croton- ate (pt./100 pts. mono- mers)	Gel (%)	Swelling in- dex of gel	$[\eta]$	Conversion (%)
Butadiene				
0.00	43	86	11.0	Complete
0.10	53	65	13.3	Complete
0.20	53	85	10.7	96
0.40	33	137	15.2	70
0.70	48	43	4.1	36
1.20	55	29	9.3	25
Butadiene/styrene (70/30)				
0.00	8	46	8.6	Complete
1.20	3	24	6.0	15.0

the smaller molecules in the soluble portion. This indicated at least some distribution of molecular size for alfin polybutadiene.

The incorporation of vinyl crotonate in a butadiene polymer or butadiene-styrene copolymer yielded results similar to those obtained when divinylbenzene was used, as shown in Table IX. A definite decrease of conversion with increasing concentration of cross-linking agent resulted. This effect was even greater than indicated, since for a concentration of 1.2 parts vinyl crotonate, *d* catalyst concentration equivalent to the other values resulted in zero conversion, and a higher concentration was required to raise it to the value shown. The quantity of gel seemed to remain relatively constant, while the swelling index decreased slightly with increase in cross-linking agent. The intrinsic viscosity remained more nearly constant than in the divinylbenzene system, but appeared to decrease slightly with increase of vinyl crotonate. Divinylbenzene did not affect conversion and catalyst efficiency as much as vinyl crotonate. This effect may of course be partially or wholly due to the impurities in the materials and not a result of the materials themselves.

Values for a butadiene-styrene copolymer are included in Table IX. The decrease of gel when a change from a butadiene to a butadiene-styrene system is made is shown. A further decrease of gel with vinyl crotonate is not con-

TABLE X
CIRCOSOL-2XH MASTERBATCHES

Polymer	Oil (pt./100 pts. polymer)	Product appearance
Polybutadiene	141	Slightly sticky, tough
Polybutadiene	305	Sticky, tough
Polybutadiene	528	Sticky, soft
Butadiene-styrene (76/24)	89	Nonsticky, tough
Butadiene-styrene (72/28)	300	Slightly sticky, tough
Butadiene-styrene (71/29)	521	Very sticky, soft

sidered significant, but again shows the failure of the vinyl crotonate to act as a cross-linking agent in the alfin system.

OIL MASTERBATCHING

In view of the toughness of the polymers produced from butadiene and butadiene-styrene mixtures, it was desirable to add quantities of a hydrocarbon oil to the swollen polymer mass before drying and removal of the diluent. Circosol-2XH in varying quantities was added to polybutadiene and butadiene-styrene copolymers, as shown in Table X. Wherever oil was mixed with polymer, drying was much more difficult, this effect probably accounting in part for the high conversions usually observed. In the calculation of conversions the total weight of oil added was assumed to be taken up by the polymer, and this weight was subtracted from the total weight recovered.

Upon the addition of plasticizer, the polymers became much softer and more workable. The addition of up to 100 parts of oil for polybutadiene and the copolymers of butadiene and styrene gave little if any increase of stickiness; above this concentration stickiness increased progressively. The copolymers tend to be slightly stickier than the polybutadiene for corresponding amounts of oil. The cohesion of the product with as high as 300 parts of oil remained great and even the polymers with 500 parts of oil were not so fluid that they could not be handled readily.

The addition of a plasticizer to the polymerization medium before reaction had taken place resulted in a polymer identical in appearance to that produced by adding oil to the swollen material. It was found that the addition of the oil decreased the efficiency of the catalyst, Sundex-53 being much more effective in this regard than Circosol-2XH. Butadiene-styrene mixtures polymerize as well as butadiene in the presence of the added oil. Some typical polymers and polymer appearances are shown in Table XI.

Its addition to the medium results in a very uniform product that requires no mixing other than shaking before the catalyst is added, but the oil must be relatively free of materials which might react with the catalyst. In the addition to the swollen polymeric mass, the purity of the oil is incidental, while uniformity of product necessitates thorough mixing, which in itself requires that the polymer be swelled to a large extent.

While the addition of Circosol-2XH to the polymerization system and to the swollen polymer mass before recovery had been satisfactory, the use of various other plasticizers in this same regard would be of definite advantage in certain applications. The addition to swollen polybutadiene of some of the more

TABLE XI
PREPARATION OF PLASTICIZER MASTERBATCH WITH CIRCOSOL-2XH

Polymer	Oil (pt./100 pts. polymer)	Product appearance
Polybutadiene	100	Spongy, tough
Polybutadiene	301	Sticky, soft
Polybutadiene	501	Very sticky, very soft
Polybutadiene	66	Tough, brown
Polybutadiene	106	Spongy, tough
Polybutadiene	227	Soft, nonsticky
Polybutadiene	770	Very sticky, very soft
Butadiene-styrene (71/29)	207	Quite sticky
Butadiene-styrene (50/50)	112	Sticky, tough
Butadiene-styrene (67/33)	153	Slightly sticky, tough

commonly used plasticizers in a concentration of 100 parts per 100 parts of polymer was tried. Compatibility or mutual adsorption of plasticizer and polymer was quite different for the various materials which were diluted with *n*-pentane and petroleum ether. Circosol-2XH is the most compatible, and readily forms a uniform nonsticky plastic mass. Trioctyl phosphate and dibutyl phthalate were quite good in this regard, while Sundex-53 was fair. BRT No. 7, Paraflux, and Bardol would not disperse readily in the solvent, and hence could not be expected to mix readily with the swollen polymer.

When these same plasticizers were added to the polymerization mixture before reaction in a concentration of 100 parts, inhibition of reaction resulted even with an excess of catalyst up to 75 per cent.

ADDITION OF FILTERS AND COMPOUNDING INGREDIENTS

In view of the difficulty of milling polybutadiene and the incorporation of carbon black into it, addition of black to the polymerization mixture or to the swollen polymer before recovery might be of value as a means of reducing milling time. Some of the reinforcing agents which were considered to be most important were tested in the polymerization system to see how they affected catalyst efficiency. The various materials charged in a concentration of 50 parts per 100 parts of butadiene are shown in Table XII with the quantity of

TABLE XII
POLYMERIZATION IN THE PRESENCE OF FILLER

Filler	Dispersion of catalyst (grams)	Conversion (%)	pH of Filler
None	3.50	62	—
—	4.53	100	—
—	4.90	100	—
Vulcan-3	7.08	53	8.5
Vulcan-3	7.28	100	—
Pelletex	6.49	100	9.7
Pelletex	7.01	100	—
NBS black	7.10	24	3.8
NBS black	8.21	42	—
Philblack-A	6.79	10	9.7
Philblack-A	7.29	17	—
Philblack-O	5.20	48	9.1
Philblack-O	5.97	100	—
Philblack-O	6.64	100	—
Philblack-O	7.92	100	—
Lignin	7.24	0	Acid
Vulcan 3 ^a	7.18	100	—
Vulcan 3	7.28	100	—
Philblack-O ^a	5.86	98	—
Philblack-O	5.97	100	—

^a Two parts KOH/100 parts of monomers.

catalyst used and the conversion. In a few of the tests shown, where a different catalyst was used, an equivalent weight of that used most often is given so that all quantities may be compared as if the same catalyst were used throughout. Of the various materials tested Philblack-O and Peletex decreased the efficiency of the catalyst the least. Pelletex may be better than Philblack-O in this regard, but was not further tested. The other blacks in their present form are considered of little value, since the efficiency of the catalyst is impaired to such an extent. In the case of lignin no reaction occurred. Vulcan-3 was a fluffy black and was the only one used in this form. The only apparent difference in the dried product resulting between the two types was that it did not rub off during handling as did the others. Except for Philblack-A which appeared anomalous, the pH of the filler seemed to correlate with catalyst efficiency—the higher the pH the higher the efficiency. Thus with Philblack-O and Pelletex, which are alkaline, the catalyst efficiency is impaired to a lesser extent than with an acid black such as NBS black.

Table XIII shows that, for Philblack-O, the higher the concentration of black, the greater quantity of catalyst was required for a given conversion.

TABLE XIII
EFFECT OF FILLER ON CATALYST REQUIREMENTS

Pt./100 pts. monomers		Dispersion of catalyst (grams)	Conversion (%)
Philblack-O	Circosol-2XH		
0	—	4.53	100
60	—	4.83	30
100	—	5.16	29
100	—	7.17	37
60	50	6.76	51
60	50	8.10	82

Also included are some tests showing catalyst requirements for a mixture of butadiene, Philblack-O, and Circosol-2XH. While the absolute increases in catalyst requirement were in some doubt because of the limited data available, the trends are distinct, and the increases in catalyst requirement for the two systems compared to the butadiene system are shown in Table XIV for given conversions. From these data the addition of 50 parts of Philblack-O increases the catalyst requirement by approximately 50 per cent, while the further addition of 50 parts of Circosol-2XH raises it another 50 to 60 per cent. Thus it must be concluded that, while advantages may result from the incorporation of

TABLE XIV
CATALYST REQUIREMENT FOR GIVEN CONVERSIONS

Conversion (%)	Catalyst required (%) for system	
	50 pts. Philblack-O	60 pts. Philblack-O/ 50 pts. Circosol-2XH
70	50.8	109.6
80	47.4	112.1
90	44.1	114.7

reinforcing agents and extenders into the polymerization medium, they are offset to some extent by an increase in catalyst requirements.

While the polybutadiene is very tough, on drying it will mill into a platic sheet with difficulty, but shears in the Mooney machine. The addition of plasticizer (Circosol-2XH) definitely lowers the Mooney viscosity, as shown in Table XV. At the same time milling is much easier. In all cases the decrease in intrinsic viscosity with milling may be noted. The decrease of gel with milling for the very tough polymer becomes an increase for the polymer with the highest oil content.

PHYSICAL TEST RESULTS

Samples for testing were prepared in 32-ounce bottles, and the products from several were pooled to yield the final blend. The methods of polymerization and the handling of the polymers consisted of conducting the polymerization in

TABLE XV
EFFECT OF PLASTICIZER ON MOONEY VISCOSITY

Oil (pts./100 pts. monomer)	Before milling		After milling		Mooney viscosity (ML/4)
	$[\eta]$	Gel (%)	$[\eta]$	Gel (%)	
117.0	11.7	26	8.0	33	22
56.6	12.3	23	6.4	25	66
0.0	18.8	22	10.4	5	Very high

dilute hydrocarbon medium to which the compounding ingredients might be added, either before or after reaction. The reaction was stopped by an alcoholic solution of phenyl- β -naphthylamine, and the polymer was recovered by kneading in water, washing, and drying. The physical conditions varied from horny dry polymers to sticky masterbatches, depending on the amount of plasticizer. Some of the black masterbatches gave evidence of poor dispersion in that the black readily rubbed off.

The polymerization data for those submitted for testing are in Table XVI. Unexpected variations in conversion, viscosity, and gel make the polymers scarcely comparable, but inasmuch as the viscosity is always high, the gel rea-

TABLE XVI
POLYMERS TESTED

Polymer no.	Butadiene-styrene charge ratio	Bound styrene (%)	Conversion ^a (%)	Gel (%)	[η]	Circosol-2XH (pts./100 pts. rubber)	Carbon black (pts./100 pts. MB rubber)	Stearic acid (pts./100 pts. oil plus rubber)
63	100/0	—	101	55	16.5	—	—	—
64A	100/0	—	112 (106)	8 ^b	17.2 ^b	—	—	—
64B	100/0	—	92 (90)	8 ^b	10.6 ^b	146	—	—
70	100/0	—	89 (79)	48	10.6	105	—	—
72	90/10	10	104	41	9.2	—	—	—
73	80/20	23	78	22	10.7	—	—	—
74	70/30	36	69	9	8.6	—	—	—
80	80/20	21	106 (100)	17	9.4	65	—	—
81	70/30	28	116 (105)	4	7.9	68	—	—
82	90/10	10	89 (81)	40 ^a	10.7 ^a	99	—	—
85	90/10	3	79 (69)	2 ^a	8.7 ^a	115 ^c	—	—
87	80/20	9	69 (63)	23 ^a	10.4 ^a	103 ^c	—	—
89	70/30	15	73 (68)	0 ^a	9.7 ^a	95 ^c	—	—
94	100/0	—	93 (93)	43 ^a	5.9 ^a	108	—	—
			—	52	14.6	—	—	—
96	100/0	—	88 (78)	47 ^a	10.4 ^a	102 ^c	—	—
			—	72	17.1	—	—	—
113	80/20	—	88	—	—	—	109 ^d	—
114	100/0	—	70	—	—	—	64 ^{c,d}	—
116	100/0	—	100	—	—	60 ^c	35	—
117	100/0	—	56	—	—	89 ^c	37 ^c	—
118	80/20	—	83	—	—	—	33 ^c	—
126	100/0	—	78	—	—	—	57	3.4
130	80/20	21	110	24	8.0	—	—	—
132	80/20	—	97	46	9.7	—	—	3.0
133	80/20	—	91	—	—	—	38	3.2

^a After extraction; values in parentheses in percentage conversion column.^b Dried at room temperature.^c Added before polymerization; otherwise after.^d Vulcan-3M; otherwise Philblack-O.

sonably low and loose, and the conversion high, these may not be too serious deficiencies. The greatest difficulty is in the ratio of rubber to masterbatching ingredients, which was in error when the conversion was unexpectedly low. This led to difficulties in compounding and testing which have been alleviated by ignoring the oil content and testing as a masterbatch by adding black on the basis of oil plus rubber (Table XXII) and by ignoring black and adding oil based on the rubber (Table XXIII).

The compounding information on the pure polymers is given in Table XVII, where it is shown that ease of processing is improved by incorporation of styrene into the charge. Black and stearic acid were 50 and 2.0 parts per 100 parts of rubber, respectively.

The compounding of oil masterbatches is described in Table XVIII. The processing was improved by the incorporation of oil, whether before or after polymerization. Incorporation of oil before polymerization resulted in a lower bound styrene at the lower conversions; hence polymers so prepared cannot be compared with others of the same charge ratio except at high conversions. Black was 50 parts per 100 parts of masterbatch and stearic acid 2.0 parts per

TABLE XVII
MILLING CHARACTERISTICS OF PURE POLYMERS

Polymer no.	Charge ratio	Milling characteristics
63	100/0	Crumbly
72	90/10	Crumbly
73	80/20	Slightly more plastic
74	70/30	Easier to process

TABLE XVIII
MILLING CHARACTERISTICS OF OIL MASTERBATCH

Polymer no.	Charge ratio	Circosol-2XH/ 100 pts. rubber	Stearic acid	Milling behavior
			added on mill/100 pts. rubber and oil	
Oil added after polymerization				
64A	100/0	82	1.1	Banded with difficulty
64B	100/0	146	0.8	Banded, nervy
94	100/0	108	0.96	Slightly crumbly
82	90/10	99	1.00	Coherent mass
80	80/20	65	1.22	Coherent mass
81	70/30	68	1.20	More plastic
130	80/20	60 ^a	1.20	Tough band
Oil added before polymerization				
70	100/0	105	0.98	Elastic band
96	100/0	101	1.00	Adherent mass
85	90/10	115	0.72	Gummy film
87	80/20	103	0.98	Nervy mass
89	70/30	95	1.02	Nervy mass

^a 60 parts added on the mill.

100 parts of rubber in the masterbatch or the amounts indicated per 100 parts of rubber plus oil.

The compounding of black masterbatches is shown in Table XIX. No great difficulties arose from this procedure except in milling, which was extremely difficult until the temperature was raised. More detail is desirable on the mill-

TABLE XIX
MILLING CHARACTERISTICS OF BLACK MASTERBATCH

Polymer no.	Charge ratio	Added on mill to total parts of					Milling characteristics
		Circosol-2XH/100 pts. rubber	Black/100 pts. rubber and oil	Circosol-2XH/100 pts. rubber	Black/100 pts. rubber and oil	Stearic acid/100 pts. rubber and oil	
Black added after polymerization							
113	80/20	0	109	60	None	1.26	Tough, rough
Black added before polymerization							
114	100/0	0	64	60	None	1.26	Shreds
118	80/20	0	64	None	None	1.90	Smooth band
118	80/20	0	54	89	57	1.06	Smooth band
Oil and black added after polymerization							
116	100/0	60	45	None	None	1.26	Rough sheet
Oil and black added before polymerization							
117	100/0	89	57	None	None	1.06	Smooth band
Black and stearic acid added after polymerization							
133	80/20	0	38	60	50	1.2	Smooth sheet
126	100/0	0	57	60	None	1.25	Smooth sheet
132	80/20	0	0	60	50	1.2	Banded

TABLE XX
COMPOUNDING RECIPE

	Parts
Polymer	100
Philblack-O	50/100 parts oil plus rubber
Stearic acid	2
Zinc oxide	5
Santocure	1.25/100 parts rubber only
Sulfur	2.0

TABLE XXI
PHYSICAL TEST DATA FOR ALFIN POLYMER

Polymer no.	Charge ratio	Cure (min. at 292° F)	Tensile strength (lb./sq. in.)	Modulus		Elongation (%)
				100% lb./sq. in.	300% lb./sq. in.	
63	100/0	— ^a	— ^a	— ^a	— ^a	— ^a
72	90/10	35	2450	680	—	260
73	80/20	15	4310	—	3010	380
74	70/30	20	4180	—	2740	260

^a No successful compound.

ing characteristics of these polymers, but since the polymers cannot be considered as ideal or representative, no greater detail is recorded at this time. Circosol-2XH, black, and stearic acid were added as far as possible to give 60 parts per 100 parts of rubber, 50 parts per 100 parts of rubber plus oil, and 2.0 parts per 100 parts of rubber, respectively.

The compounding recipe used was that shown in Table XX. The Polymer was considered rubber plus oil. The black was adjusted to be 50 parts per 100 parts of rubber or masterbatch. All the other ingredients were adjusted to give the amounts shown per 100 parts of rubber.

The physical test data on the pure polymers compounded as in Table XVII are given in Table XXI. It can be seen that when compounding was made

TABLE XXII
PHYSICAL TEST DATA FOR OIL MASTERBATCH

Polymer no.	Charge ratio	Cure (min. at 292° F)	Tensile strength (lb./sq. in.)	Modulus		Elonga- tion (%)
				100%, lb./sq. in.	300%, lb./sq. in.	
Oil added after polymerization						
64A	100/0	50	2865	200	1490	460
64B	100/0	50	2040	—	680	560
94	100/0	15	1745	—	—	210
82	90/10	50	2260	—	620	650
80	80/20	50	2700	—	1050	540
81	70/30	100	2210	—	690	600
Oil added before polymerization						
70	100/0	50	1610	290	800	550
69	100/0	25	2410	—	1090	500
85	90/10	35	1630	—	490	640
87	80/20	50	2670	—	430	710
89	70/30	50	1845	—	360	730
130	80/20	35	2685	—	890	610

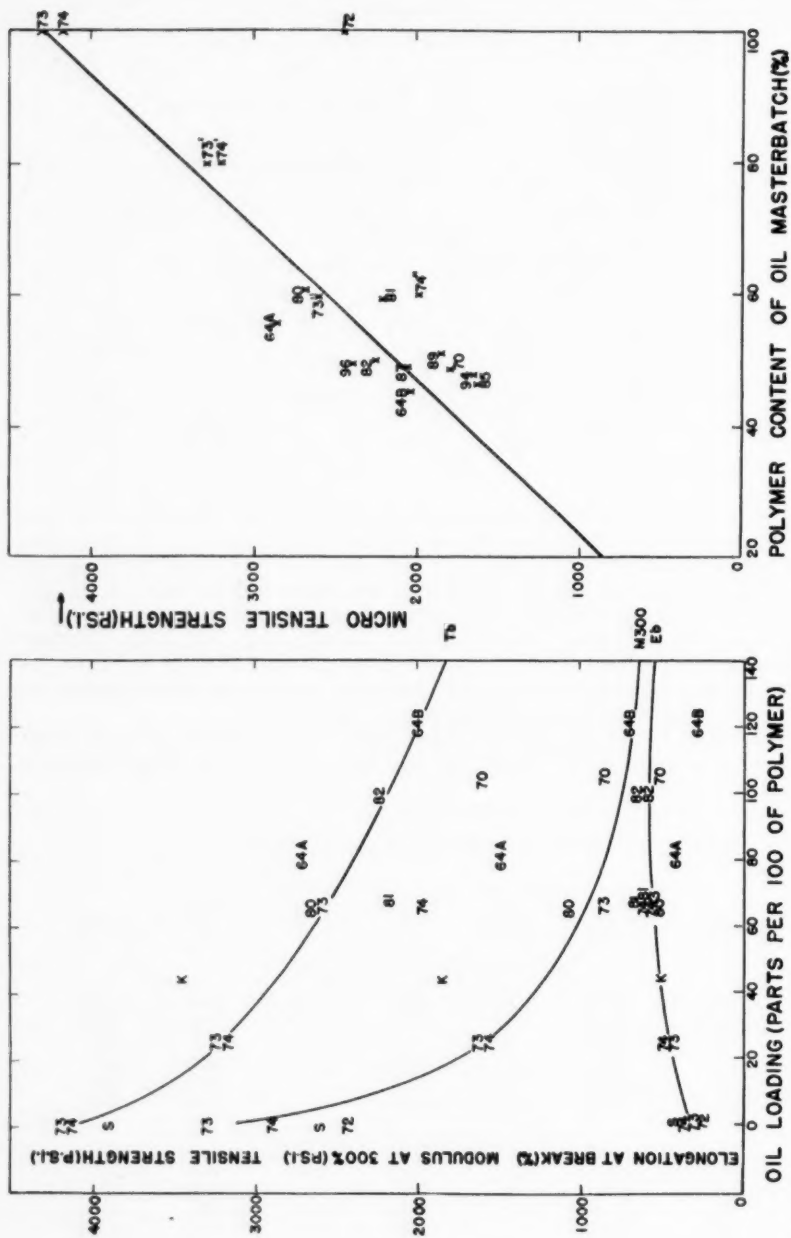


Fig. 2A.—Ultimate tensile strength, elongation, and modulus at 300% elongation of alpha polymers with various amounts of oil per 100 parts of polymer.

Fig. 2B.—Ultimate tensile strength related to the percentage polymer in polymer-oil masterbatch.

possible by copolymerization of butadiene and styrene, good tensile strengths were obtained. The modulus was also very high. Generally speaking, although desirable tensile strengths were obtained, the processing was most difficult.

The physical test data for the oil masterbatches compounded as in Table XVIII are given in Table XXII. There would appear to be little difference between masterbatches prepared by adding the oil to the finished polymerization mass and adding it before polymerization to the medium. The tensile strengths ranged from about 3000 pounds per square inch for a masterbatch containing about 50 parts of oil to 2000 pounds per square inch for masterbatches containing 100 parts of oil. The processing was improved, but was still difficult. In Figure 2, B, the data are plotted on the basis of percentage of oil in the masterbatch and show a remarkable tendency toward linearity. The

TABLE XXIII
PHYSICAL TEST DATA FOR BLACK MASTERBATCH

Polymer no.	Charge ratio	Cure (min. at 292° F)	Tensile strength (lb./sq. in.)	Modulus		Elongation (%)
				100%, lb./sq. in.	300%, lb./sq. in.	
Black added after polymerization						
113	80/20	100	810	330	—	200
Black added before polymerization						
114	100/0	20	610	340	—	200
		50	1960	—	730	500
118	80/20	25	2630	—	—	200
Oil and black added after polymerization						
116	100/0	35	1840	720	—	360
Oil and black added before polymerization						
117	100/0	35	1835	—	1030	460
Black and stearic acid added after polymerization						
133	80/20	50	2760	—	590	680
126	100/0	20	1270	—	690	550
132	80/20	70	2630	—	860	600

points for polybutadiene tend to be at the top of the scatter and the points are lower as the styrene content of polymer is increased for a constant oil loading.

The physical test data for the black and stearic acid masterbatches compounded as in Table XIX are given in Table XXIII. Again no marked changes were noted. Polymers 113 and 114 appeared to have become gelled beyond recovery.

It can be concluded that physical properties are not altered greatly by methods of incorporating oils, black, or stearic acid, but that process advantages or processing advantages may be gained by such techniques. Various limited compounding studies were conducted on the polymers listed in Table XVII.

Polymers 73 and 74 were mill mixed with various amounts of Circosol-2XH and the results in Table XXIV obtained. They serve to illustrate the rapid decrease in tensile strength and modulus with oil loading.

TABLE XXIV
PHYSICAL TEST DATA FOR MILL-MIXED ALFIN OIL BLENDS

	Polymer 73			Polymer 74		
Polymer, parts	50	40	30	50	40	30
Circosol-2XH	0	10	20	0	10	20
Cure (min. at 292° F)	12	15	35	20	25	35
Tensile (lb./sq. in.)	4310	3260	2610	4180	3200	1995
Elongation (%)	380	500	600	2740	510	660
Modulus (300%)	3010	1530	600	400	1480	570

DISCUSSION

The polymerization behavior of the system from these studies is very similar to reported data. The catalyst has been found to be effective under conditions which would likely be met in commercial practice using technical grade materials. A usable polymer would appear likely to contain about 20 per cent bound styrene and about 50 to 100 parts of a plasticizer for most applications, although the system is capable of producing a wide variety of copolymers and masterbatches of varying characteristics. The effects of diluents or plasticizers may be overcome by changes in dilution or polymerization temperature.

Polymerization in the presence of plasticizers is possible, and may represent one means of improved production and handling of the copolymer. When certain oils are used, the catalyst requirements are increased. Some of the oils are such that this increase is not unreasonable.

Of most interest at this time is the apparent linear relationship between the percentage polymer in the masterbatch and the tensile strength. A similar observation was made several years ago¹¹ based on the fractionation studies of many polymers of widely varying Mooney values. The percentage polymer with a dilute solution viscosity of less than one was determined. This corresponds to the fraction with a molecular weight¹² of less than 100,000. These data are plotted in Figure 3 in the form of percentage polymer over an intrinsic viscosity of one *vs.* the tensile strength. The line below is that from Figure 2,

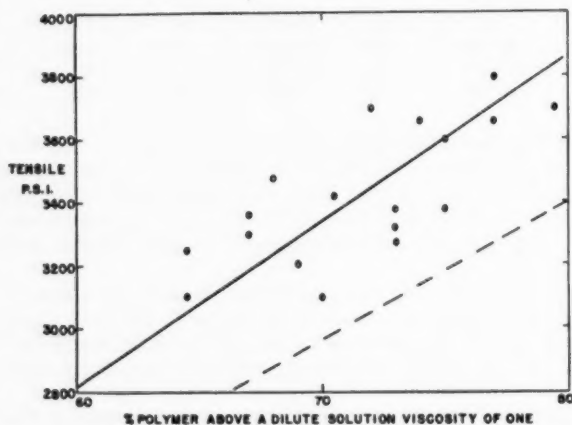


FIG. 3.—Ultimate tensile strength of a series of GR-S-Type polymers related to the percentage of raw polymer having a dilute solution viscosity over 1. Lower dashed curve is from Figure 2, B.

B. It can be seen that a simple shift of the top line would bring it very close to the lower. Such a shift is accomplished by accepting polymer of an intrinsic viscosity of over 0.5 as rubberlike and below that value as plasticizerlike, as observed by Yanko¹³. The data of Yanko suggest that just such an assumption will bring the two systems into coincidence, since this represents approximately a 10 per cent increase of the rubbery portion of GR-S polymer.

SUMMARY

Alfin catalysts, as developed by Morton, have been used for a study of the polymerization reactions of butadiene-styrene, and other monomers. Catalyst activity was affected by minor variations in the method of preparation and increased during the first few days of storage of the catalyst. Water, alcohols, and ketones acted as catalyst poisons. Technical pentane and crude propylene streams can replace the normally pure materials used in the preparation of the catalyst.

Copolymers of butadiene with styrene or α -methylstyrene were slightly richer in the styrene than the corresponding emulsion copolymers, except when Circosol-2XH was present in the medium. This resulted in polymers less rich in styrene. Attempts to induce cross-linking by incorporation of vinyl crotonate or divinylbenzene into the polymers did not result in a tighter gel.

In the polymerization of butadiene, there is a threshold concentration of catalyst below which no reaction occurs and above which the final conversion obtained rises rapidly to 100 per cent with increased catalyst concentration. The lower the concentration of inert diluents in the reaction system, the lower the threshold value. The intrinsic viscosity of the polymer increases as reaction temperature is raised and decreases as conversion proceeds. Intrinsic viscosities over 20 can be obtained. In contrast, butadiene-styrene copolymers increase in intrinsic viscosity as conversion is increased and have a lower gel content. The intrinsic viscosity of the copolymers is much lower than for the polybutadiene samples and the catalyst requirement is higher.

Polymerization will occur in the presence of butanes and butylenes, hydrocarbon oils such as Circosol-2XH, carbon black, and stearic acid although the catalyst requirements are thereby increased. Incorporation of such materials before or immediately after polymerization markedly improves the processability of the polymers. Physical evaluation of resulting masterbatches has indicated retention of desirable properties.

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SUMMARY

Alfin catalysts offer a distinctly new method of producing a very tough synthetic rubber, which previous studies had shown to have some properties superior to GR-S. The oil masterbatching technique enabled the rubber to be blended with plasticizer in sufficient quantities to render this tough polymer processable. Thus a study was undertaken of the polymerization variables in

the system in order to lay a firm foundation for pilot plant development of the process.

It was found that the catalyst could be prepared in satisfactory activity using commercial materials rather than high grade chemicals. Although several monomers appeared to be polymerized or copolymerized readily using this catalyst, by far the best results were obtained with butadiene or butadiene and styrene. Highly purified butadiene was not required for the process. The reaction proceeded rapidly at room temperature, although the rate could be increased by an increase in temperature. More efficient utilization of catalyst could be achieved by lower dilutions of the monomers. Polymerization also could be conducted in the presence of plasticizers or carbon black, or these materials could be masterbatched with the final polymer while it was still swollen by the diluent.

Successful continuous polymerization by alfin catalysts to yield a processable polymer of acceptable quality should be possible by a comparatively inexpensive process, which has the additional virtue that highly purified butadiene, which has been the cause of several recent serious explosions, will not be required at any stage of the process.

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MECHANISM OF THE ACTION OF INHIBITORS OF THE OXIDATION OF ELASTOMERS *

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A number of works have been published in the recent scientific literature concerning the action of antioxidants in elastomers. Most of these works are of an empirical nature and are of purely practical value.

In certain foreign works, unsuccessful attempts were made to relate the effectiveness of action of antioxidants with one of their specific properties, for example, with their oxidation-reduction potential¹.

The mechanism of inhibited and of free oxidation of elastomers was studied in detail by one of the present authors². Based on a theory of chain reactions, Semenov concluded that the oxidation of rubber involves a chain degradation process, and he showed that the inhibitor, phenyl- β -naphthylamine, breaks the oxidation chains, reacting with the peroxidic radicals which are formed in the rubber molecules during oxidation. The inhibitor is consumed by union with the hydrocarbon molecule. Consumption of inhibitor during heat treatment of rubber is observed only in the presence of oxygen.

In the light of our theories of the oxidation of rubber, and also on the basis of contemporary theories of the activity of radicals, according to which the more active molecules in the radical reactions form less active radicals, and vice versa, the mechanism of the action of inhibitors can be described as follows. The peroxide radicals of the rubber detach the more active or mobile hydrogen from the inhibitor molecule, and the radical formed as a result of this reacts with the rubber radicals, breaking the oxidation chains.

Effective inhibitors, reacting with the peroxide radicals of the rubber, must rupture the entire oxidation chain, that is, they do not cause any chain transfer.

A number of substances, for example, sulfur and accelerators, considered at present to be inhibitors of the oxidation of rubber, are in reality only regulators of the process, since, during the reaction with the rubber radicals, new radicals are formed which still possess sufficient activity to extend the chain.

Those observations enable us to establish the basic requirements for a substance to be an inhibitor. The inhibitor molecule must be sufficiently active to react with the peroxidic radical and the new radical thus formed must possess a very small reactivity. On the other hand, the activity of the inhibitor with respect to molecular oxygen must be negligible; if not, it may be consumed ineffectively. If the inhibitor is oxidized more easily than is the rubber hydrocarbon, then it will act as a negative catalyst of the oxidation of rubber.

In this work the first experimental results of an investigation of the mechanism of the action of inhibitors on the oxidation of rubber are presented. Phenyl- β -naphthylamine and some of its derivatives were used as inhibitors. The experiments were carried out with hydrocarbons of natural rubber and sodium-butadiene copolymers.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Doklady Akademii Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik*, Vol. 82, No. 5, pages 747-750, 1952.

First of all we studied the relation between the molecular structure of the inhibitor and its inhibiting power. The action of a given inhibitor is characterized by the length of the induction period of the oxidation of rubber when it is present.

With the aim of establishing the most active or mobile hydrogen atom in the phenyl- β -naphthylamine molecule which takes part directly in the reaction

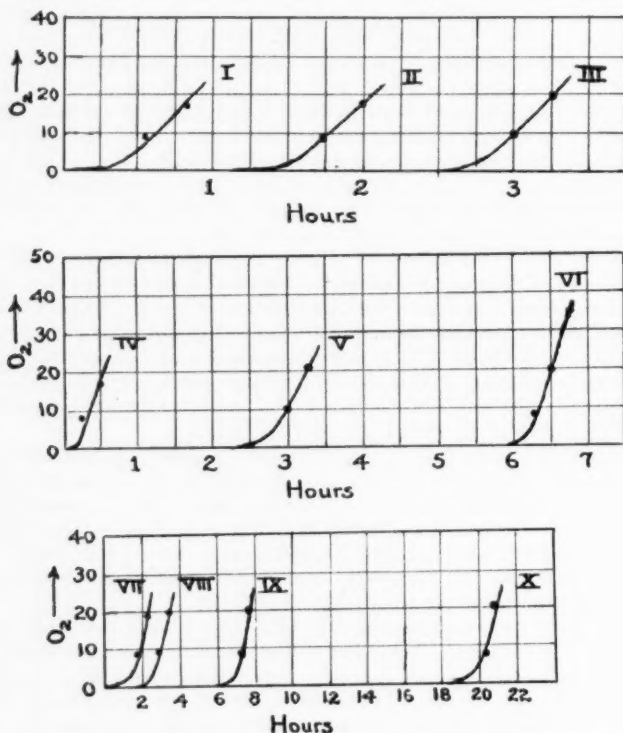


FIG. 1.—Kinetics of oxidation of natural rubber hydrocarbon by molecular oxygen at 130° C in the presence of 10 millimoles of inhibitor per mole of rubber hydrocarbon.

- I with methyl- β -naphthylamine
 - II with phenyl- α -methyl- β -naphthylamine
 - III with phenyl- β -naphthylamine
 - IV with diphenylamine
 - V with phenyl- β -naphthylamine
 - VI with β,β -dinaphthylamine
 - VII with *n*-tolyl- β -naphthylamine
 - VIII with phenyl- β -naphthylamine
 - IX with *n*-chlorophenyl- β -naphthylamine
 - X with *n*-hydroxyphenyl- β -naphthylamine
- O₂ amount of oxygen absorbed in millimoles per mole of rubber

with the peroxidic radical, we synthesized two derivatives of phenyl- β -naphthylamine, viz., α -methylphenyl- β -naphthylamine and tertiary-methylphenyl- β -naphthylamine.

Comparison of the inhibiting activity of these compounds with phenyl- β -naphthylamine when added to rubber in equimolecular amounts showed that

the displacement of the α -hydrogen, as well as that of the amine-hydrogen, lowers greatly the inhibiting action of the compound (Figure 1, curves I, II, and III). From this it may be concluded that the power of an inhibitor is governed by both hydrogen atoms. Clearly in this case there is a mutual influence.

Extremely interesting results were obtained when the behavior of such inhibitors as diphenylamine, phenyl- β -naphthylamine and β,β -dinaphthylamine were compared.

Figure 1 (curves IV, V, and VI) shows the corresponding kinetic curves, from which we see that the activity of inhibitors increases sharply with the complexity of the molecule, in the order: diphenylamine, phenyl- β -naphthylamine, and dinaphthylamine. This fact accords with general theories of the strength of the chemical bond, which decreases with increase of the number of bonds within the molecule. This is related to the greater dislocation of the electron cloud. On the other hand, a change of the number of α -hydrogen atoms in the molecule from none (in diphenylamine) to two (in dinaphthylamine) can also cause a corresponding change of length of the induction.

It is known that the mobility or activity of the hydrogen atoms in the phenyl ring is strongly influenced by the substituent in *para*-position. We synthesized *n*-hydroxyphenyl- β -naphthylamine, *n*-chlorophenyl- β -naphthylamine, and *n*-tolyl- β -naphthylamine.

A comparison of their inhibiting power is given in Figure 1 (curves VII, VIII, IX, and X). As is evident, the effect of the methyl group is reflected by a decrease of the inhibiting effect of phenyl- β -naphthylamine, and that of the hydroxyl group and chlorine is reflected in an increase. These experimental data are in complete agreement with contemporary views of the strength of the chemical bond; the radical-hydrogen bond is reinforced by the more electropositively charged substituent and is weakened by the more electronegatively charged substituents.

In explaining the mechanism of action of an inhibitor, a question of great interest is what influence the inhibitor exerts on the newly formed stable peroxides of rubber. In the investigation of the reaction of various inhibitors with stable peroxides of rubber, the following observations were made.

The rate of decomposition of peroxides of sodium-butadiene rubber in an atmosphere of nitrogen at 80° C for twelve hours was no different when phenyl- β -naphthylamine was present.

Consequently under these conditions phenyl- β -naphthylamine does not react with the stable rubber peroxides.

When *n*-hydroxydiphenylamine, *n*-hydroxyphenyl- β -naphthylamine, or trihydroxybenzene is added to a rubber solution containing stable peroxides, the mixture very rapidly acquires an intense yellow color. When these compounds are added to a solution of unoxidized rubber, no color changes are observed. This indicates that the compounds mentioned above, in contradistinction to phenyl- β -naphthylamine, react with the stable rubber peroxides.

It is, therefore, reasonable to assume that amino compounds and hydroxy compounds (or hydroxyamino compounds) behave differently toward the stable rubber peroxides. Whereas the former react with the peroxide radicals, the latter destroy the stable peroxides and peroxide radicals which are formed. Since, during the oxidation of rubber, both stable peroxides and peroxide radicals are formed, the use of a combination of inhibitors of the two classes

indicated should lead to complete suppression of the oxidation process and, consequently, should be a very effective method of compounding.

ACKNOWLEDGMENT

The authors consider a pleasant duty the expression of their gratitude to A. D. Abkin for valuable suggestions.

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VULCANIZATION CHARACTERISTICS OF NATURAL RUBBER *

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The present classification program for natural rubbers has been handicapped by the lack of adequate means to characterize their behavior on vulcanization. Several methods have recently been proposed for this purpose. Roth and Stiehler¹ described the strain test from which three vulcanization parameters can be calculated. Two of these parameters have been combined by Schade². Thirion³ proposed a method for calculating two parameters from the customary measurements of stress at 600 per cent elongation. Gee and Morrell⁴ have recently suggested a procedure for determining two parameters from measurements of Mooney viscosity and stress at 100 per cent elongation. Workers at The B. F. Goodrich Company⁵ have proposed the use of the Mooney viscometer for determining two parameters.

The present study was initiated to compare these methods for classifying natural rubbers. At the same time, an investigation was made of several conditions of treatment of the compound before vulcanization and of the temperature of vulcanization to determine their relative effects on the parameters and the classification of the rubbers.

For this work, four Hevea rubbers that covered a wide range in both rate of cure and ultimate stiffness of the vulcanizate were chosen. The rubbers were smoked sheet, pale crepe, sprayed latex, and Tensorub. The sample of smoked sheet was from a bale of No. 1 grade rubber, taken at random. The same was true for pale crepe. The sample of sprayed latex rubber was prepared by the U. S. Rubber Co. plantation by spray-drying once-creamed formaldehyde-preserved latex. The sample of Tensorub was produced by Socfin Co., Ltd., in Malaya and was selected to represent a high-quality smoked sheet.

EXPERIMENTAL PROCEDURE

The American Chemical Society's No. 1 recipe⁶, which is now being used for the Technical Classification of natural rubbers, was used in this investigation. The batch size was five times the formula weight in grams. The compounds were mixed on a laboratory mill having rolls 6 inches in diameter and guides spaced 10.5 inches apart. The speed of the front roll was 24 r. p. m. and of the back roll 33.6 r. p. m. The temperature of each roll was recorded and controlled automatically, using thermocouples embedded in the roll for the sensing element. The temperature of the rolls was maintained at $70^{\circ} \pm 2^{\circ}$ C. The ambient temperature and humidity were maintained constant at 25° C and 35 per cent. The procedure used to mix the compounds follows:

* This paper is a reprint from Special Publication No. 138 of the American Society for Testing Materials. The paper was presented at a meeting arranged by Committee D-11 on Rubber and Rubberlike Materials, and comprising a "Symposium on the Evaluation of Natural Rubber", in New York, N. Y., June 26, 1952.

1. Pass the rubber twice between the rolls with the clearance between them set at 0.008 in. 2 min.
2. Band and mill with roll clearance set at 0.065 in. 1 min.
3. Open the rolls to a clearance of 0.090 inch and make four cuts three-fourths of the distance across the rolls, alternating from one side to the other at 15-sec intervals. 1 min.
4. Add the compounding ingredients. 2 min.
5. Make eight cuts three-fourths of the distance across the rolls, alternating from one side to the other at 15-sec. intervals. 2 min.
6. Cut the batch from the mill and pass it three times between the rolls with the clearance set at 0.030 in. 1 min.
7. Band and mill with the roll clearance set at 0.090 inch. Make eight cuts in the same way as in step 5. 2 min.
8. Sheet off the batch with the roll clearance set at 0.120 in. $\frac{1}{2}$ min.
- Total time. 11 $\frac{1}{2}$ min.
9. Check the batch weight.
10. Cut specimens for two Mooney viscosity determinations and seven slabs for curing.
11. Place all pieces in an air-tight container until ready for testing or curing.

Before testing or curing, the compounds were treated in the following ways. In one experiment, they were allowed to rest overnight in the airtight container before measurement of Mooney viscosity and curing. In a second experiment,

TABLE I
TREATMENT OF COMPOUNDS

Treatment ^a	Temperature of cure, (deg. Cent.)	Storage before curing		Day of mixing	
		Humidity	Time	Batch A	Batch B
125 DR	125	Low	Overnight	February 28	March 27
125 HR	125	High	Overnight	March 20	April 17
125 D	125	Low	Minimum	March 7	April 4
140 D	140	Low	Minimum	March 14	April 11

^a The letters D, H, and R designate, respectively, dry, humid, and rest.

they were similarly treated except that a salt solution was present in the container which at equilibrium gave a relative humidity of 95 per cent. In the third and fourth experiments, they were measured and cured within a few hours after mixing. In the first three experiments, Mooney viscometer cure measurements and vulcanization of sheets for stress-strain measurements were conducted at 125° C. In the fourth experiment, they were conducted at 140° C. In all four experiments, Mooney viscosity was measured at 100° C and standard 6- by 6-inch sheets were cured for 180, 90, 45, 30, 20, 15, and 12 minutes in the order listed. The sheets were cured in chromium-plated mold cavities that were machined into the steam plate of the hydraulic press. Each experiment was repeated after an interval of four weeks. Table I summarizes the conditions for the four treatments and gives the dates on which each batch was mixed.

TESTS

After a 1-minute warm-up period, the Mooney viscosity both at 100° C and at curing temperature was automatically recorded, using for the pick-up a

linear-transducer attached to the stem of the dial gauge. The temperature was measured automatically by means of thermocouples, embedded into both the upper and lower dies, and a recorder. The standard rotor 1.5 inches in diameter was used in all instances. All values were read from the recorder charts. The viscometer was run for 4.5 to 5 minutes for measurements at 100° C and until the viscosity increased 40 units or more above the minimum for measurements at curing temperature.

TABLE II
STRESS AND ELONGATION AT FAILURE

Treatment	Time of cure (min.)	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
		Stress (lb. per sq. in.)	Elongation (per cent)	Stress (lb. per sq. in.)	Elongation (per cent)	Stress (lb. per sq. in.)	Elongation (per cent)	Stress (lb. per sq. in.)	Elongation (per cent)
125 DR	12	1850	900	1570	960	2660	830	2820	820
	15	2270	865	1820	945	2470	790	3170	795
	20	2400	810	2200	900	2720	790	3380	750
	30	2880	790	2480	860	2630	750	3720	720
	45	2780	760	2640	830	2620	730	3840	700
	90	2960	740	2670	780	2580	740	3620	665
	180	2700	720	2780	785	2470	725	3300	650
125 HR	12	1940	890	1880	985	2480	815	2720	810
	15	2170	825	1980	920	2400	800	2760	785
	20	2480	815	2280	890	2580	780	3230	760
	30	2600	780	2450	850	2690	745	3420	725
	45	2740	750	2750	830	2750	780	3540	700
	90	2600	715	2580	770	2440	715	3420	660
	180	2510	710	2750	770	2620	750	3440	665
125 D	12	1700	920	1600	1005	2510	840	2590	810
	15	2040	885	1840	940	2540	820	3040	805
	20	2460	840	2200	900	2430	790	3340	765
	30	2630	790	2520	840	2660	780	3270	700
	45	2690	755	2650	830	2770	770	3450	690
	90	2570	725	2720	800	2500	740	3570	670
	180	2890	750	2730	790	2480	740	3310	650
140 D	12	2640	800	2480	860	2660	780	3380	720
	15	2610	780	2450	850	2820	785	3550	710
	20	2840	770	2520	830	2580	770	3540	700
	30	2490	735	2530	805	2560	760	3440	680
	45	2580	750	2670	810	2450	750	3370	670
	90	2440	765	2510	815	2330	750	3010	680
	180	2160	792	2520	865	2450	780	2810	705

Stress-strain measurements were made with three testers. Strain at 100 lb. per sq. in. was measured with a National Bureau of Standards' strain tester⁷; stress at 600 per cent elongation and at failure were measured with a Model ORR L-5 Scott tension testing machine; and stress at 100 per cent and 600 per cent elongation were measured with an Instron testing machine⁸. The force-measuring element is a pendulum in the Scott machine and a strain gauge in the Instron machine.

Six strips⁷ and four dumbbells⁹ were cut from each sheet of vulcanizate. Three strips were used to make N.B.S. strain measurements, and the other three were used to measure stress at 100 per cent elongation with the Instron machine. On the strips the bench marks were 10 cm. apart. Two dumbbells

were used for tests with the Scott tension testing machine and the other two for measurements of stress at 600 per cent elongation with the Instron machine. The standard 1-inch bench marks were used in both instances. The rate of jaw separation was 20 inches per minute on both the Scott and Instron machines.

STRESS AND ELONGATION AT FAILURE

Historically the time of optimum cure has been judged from the curve relating stress at failure and time of cure. Some workers have also used the product of stress and elongation at failure or the energy required to break the rubber in place of the stress at failure. Although these methods have relatively poor precision, they do offer a means for determining the state of cure. Because these methods have been found by experience to yield results in agreement with

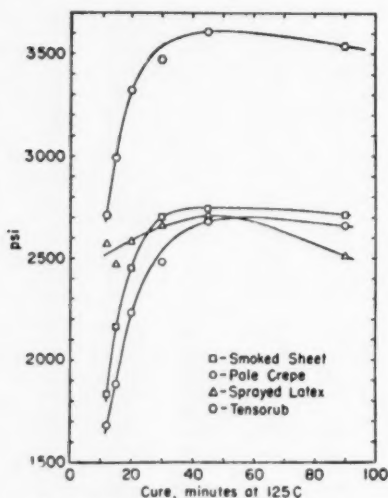


Fig. 1.—Stress at failure vs. time of cure.

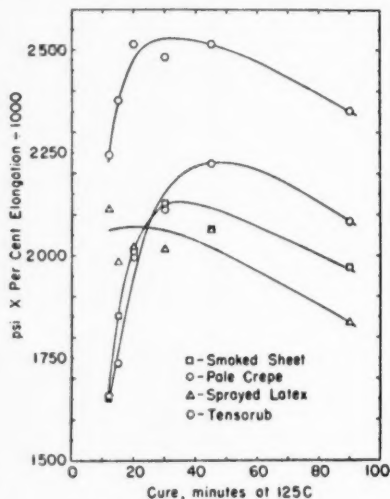


Fig. 2.—Product of stress and elongation at failure vs. time of cure.

service, any new method must agree qualitatively in characterizing rubbers in order to be generally accepted.

The average results for the duplicate mixings of each of the 16 compounds in this study are given in Table II. Several qualitative conclusions can be drawn from these data. At 140° C, vulcanizates of all rubbers cured 12 minutes have stresses at failure close to the maximum observed for any time of cure. None of the vulcanizates are undercured in the usual sense. This temperature is, therefore, too high to detect differences between the curing rates of rubbers, using stress and elongation at failure as criteria. The elongation of all vulcanizates cured 90 and 180 minutes indicates that severe reversion has occurred. At 125° C vulcanizates of the three compounds for any one rubber are not significantly different within the precision of these measurements. Consequently, they may be averaged for detecting differences between rubbers. Figure 1 compares the average stresses at failure for the different rubbers. Figure 2 shows the average products of stress and elongation at failure. These figures

show that sprayed latex rubber has reached maximum values in the shortest cure time used, and pale crepe requires the longest time. Nevertheless, it is apparent that even this rubber reaches maximum values in less than 45 minutes of cure at 125° C. Tensorub and smoked sheet are intermediate, with Tensorub requiring somewhat less time than smoked sheet. Another striking difference is the large values for Tensorub compared to those for the other three rubbers.

STRESS AT 600 PER CENT ELONGATION

Next to the stress-strain properties at failure, the stress at some specified elongation (often 600 per cent) has been most commonly used for characterizing natural rubbers. The results obtained for this property by means of both the Instron and Scott machines are given in Table III. Analysis of the data for the two machines indicates that, for specimens from the same sheet, the Instron results are about 5 per cent lower in value than the Scott results. There is a coefficient of variation of approximately 3 per cent for the Instron results and of approximately 4 per cent for the Scott results. Thus, the Instron machine appears to be somewhat more sensitive than the Scott machine for detecting differences among vulcanizates, but not as much as might be expected, since the subjective measurement of the elongation limits the precision that can be obtained.

TABLE III
STRESS AT 600 PER CENT ELONGATION, PSI

Treatment	Time of cure (min.)	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
		Instron	Scott	Instron	Scott	Instron	Scott	Instron	Scott
125 DR	12	413	412	—	250	646	732	858	917
	15	541	565	316	320	769	867	1129	1160
	20	715	742	405	442	817	895	1255	1492
	30	890	972	505	542	923	1025	1761	1972
	45	1055	1102	596	645	997	1172	2030	2235
	90	1227	1327	736	792	1075	1047	2332	2620
	180	1035	1272	734	812	862	1000	2219	2582
125 HR	12	467	487	289	293	690	780	884	920
	15	598	612	357	357	694	737	1055	1025
	20	713	750	458	455	821	875	1325	1362
	30	927	915	562	580	928	1105	1720	1765
	45	1110	1105	671	715	1012	1057	2085	2097
	90	1289	1322	836	850	1058	1147	2485	2550
	180	1238	1260	817	922	1039	1055	2503	2440
125 D	12	359	355	225	225	575	600	850	850
	15	477	487	309	325	642	687	1082	1045
	20	672	680	450	422	743	737	1421	1377
	30	887	847	581	572	858	852	1781	1772
	45	1080	1052	687	665	929	920	2183	2092
	90	1207	1165	783	745	964	988	2595	2477
	180	1191	1182	829	790	960	977	2544	2520
140 D	12	756	847	526	560	829	875	1716	1735
	15	878	902	577	565	855	872	1890	1912
	20	951	1002	639	637	844	907	2109	2142
	30	1042	1055	705	682	898	885	2211	2262
	45	1067	1067	715	727	912	880	2338	2295
	90	896	907	689	670	869	895	1917	1982
	180	697	687	577	542	766	742	1620	1540

The average results for the vulcanizates cured at 125° C are shown in Figure 3. It is seen that a longer time is required to reach maximum values of stress at 600 per cent elongation than stress at failure. Nevertheless, it is again observed that sprayed latex reaches a maximum value in the shortest time and pale crepe requires the longest time.

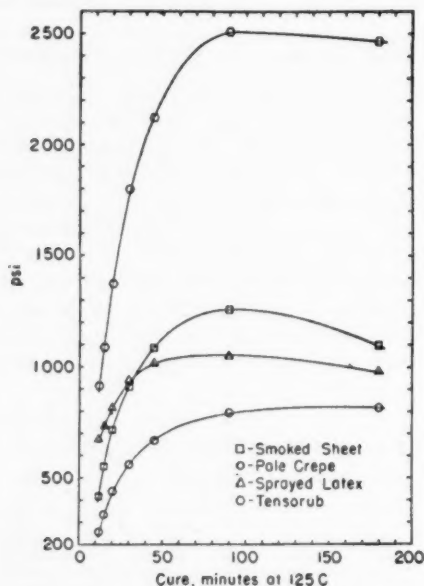


FIG. 3.—Stress at 600 per cent elongation vs. time of cure.

The method of Thirion³ was used to calculate the limiting modulus A and the time constant B for the various compounds. The values for the limiting modulus A were found to depend on the cures selected for the calculation. When the values for the 15- and 30-minute cures at 125° C were used to calculate the limiting modulus A , the relation between $\log \left(\frac{A}{A - M} \right)$ and the time of cure showed no tendency toward linearity. When the values for the 45- and 90-minute cures were used, $\log \left(\frac{A}{A - M} \right)$ was essentially linearly related to the time for the longer cures, but the curves deviated from linearity for the short cures and intercepted the time axis at positive values, presumably corresponding to the time of incipient cure. However, the intercepts could not be accurately determined.

Table IV lists for each rubber the value for limiting modulus A , calculated on the basis of the 45- and 90-minute cures and the time constant B obtained from plots of $\log \left(\frac{A}{A - M} \right)$ vs. time of cure. The value of stress at 600 per cent elongation M for each cure was obtained from the mean of the six values given in Table III for the vulcanizates cured at 125° C. The values for A are

TABLE IV
VULCANIZATION PARAMETERS (THIRION): AVERAGE VALUES
FOR COMPOUNDS CURED AT 125° C

Rubber	Limiting modulus A (lb. per sq. in.)	Time constant B (min.)
Smoked sheet	1288	24.5
Pale crepe	820	27.2
Sprayed latex	1048	13.0
Tensorub	2598	26.7

nearly the same as the stresses at 600 per cent elongation for vulcanizates cured 90 minutes shown in Figure 3. Except for sprayed latex, the time constants *B* are nearly the same, indicating that three of the rubbers have essentially the same rate of cure. This conclusion is obviously not in accord with those deduced from results of stress and elongation at failure.

STRESS AT 100 PER CENT ELONGATION

The British Rubber Producers' Research Association (B.R.P.R.A.) has recently proposed the use of stress at 100 per cent elongation in place of stress at 600 per cent elongation for characterizing natural rubbers⁴. This lower elonga-

TABLE V
STRESS AT 100 PER CENT ELONGATION, PSI

Treatment	Time of cure (min.)	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
		A	B	A	B	A	B	A	B
125 DR	12	60	63	56	53	78	78	80	87
	15	70	70	60	63	83	82	89	92
	20	75	78	66	66	85	86	97	102
	30	86	87	72	73	92	93	114	122
	45	93	97	80	80	96	96	127	132
	90	105	106	90	90	99	100	146	151
	180	106	111	94	95	103	103	146	150
125 HR	12	67	63	57	58	74	81	87	81
	15	77	70	63	63	83	82	93	88
	20	81	77	67	68	—	88	103	98
	30	88	87	77	76	92	97	120	112
	45	99	97	83	83	98	98	134	132
	90	111	107	93	95	104	103	153	145
	180	110	110	99	101	104	105	150	151
125 D	12	62	57	57	53	78	75	85	77
	15	70	63	60	58	80	80	93	87
	20	78	72	68	66	84	82	105	97
	30	88	82	76	73	91	88	120	111
	45	97	94	84	80	93	94	133	126
	90	106	102	91	90	100	99	155	145
	180	110	108	96	98	102	100	154	151
140 D	12	87	83	71	73	91	88	117	113
	15	91	88	77	77	92	90	127	120
	20	96	91	81	82	—	93	132	129
	30	100	96	87	87	101	96	139	138
	45	104	101	91	91	99	100	145	141
	80	101	100	91	92	100	102	136	134
	180	90	91	75	86	97	118	126	123

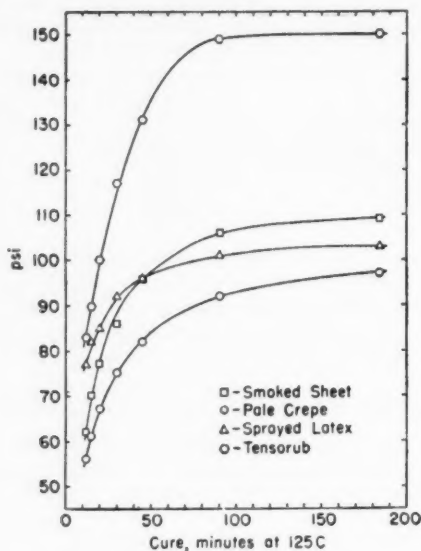


Fig. 4.—Stress at 100 per cent elongation vs. time of cure.

TABLE VI
MOONEY VISCOSITY AND VULCANIZATION PARAMETERS (B.R.P.R.A.)

	Treatment	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
		A	B	A	B	A	B	A	B
Viscosity ML— 100° C (1 + 4 min.)	125 DR	66.6	71.0	66.0	70.8	58.0*	61.4*	60.2	66.3
	125 HR	69.1	68.3	74.0	72.0	69.0*	61.3*	65.1	69.9
	125 D	70.0	68.9	74.0	70.3	56.5*	54.2*	65.8	61.2
	140 D	69.4	67.5	73.0	70.5	69.0*	57.0*	64.9	61.7
F_0 (lb. per sq. in.)	125 DR	1.1	2.0	1.0	2.0	-0.9	0.0	-0.3	1.0
	125 HR	1.6	1.4	2.3	2.1	-0.3	0.0	0.9	-0.3
	125 D	1.8	1.6	2.6	1.8	-1.3	-1.8	1.0	0.0
	140 D	1.7	1.3	2.3	1.9	-0.3	-1.1	0.9	0.1
F_{90} (lb. per sq. in., based on 15- and 30-min. cures)	125 DR	90.8	92.7	75.1	75.0	93.1	94.7	123.7	136.8
	125 HR	89.9	92.6	81.2	79.5	93.1	100.4	131.2	121.0
	125 D	94.5	90.5	82.2	78.5	92.7	88.9	131.2	120.1
	140 D	101.0	96.8	88.5	88.5	102.0	96.4	140.3	141.2
K (min ⁻¹ , based on 15-min. cure)	125 DR	0.097	0.092	0.106	0.120	0.149	0.134	0.085	0.074
	125 HR	0.128	0.093	0.098	0.103	0.148	0.113	0.082	0.087
	125 D	0.089	0.078	0.085	0.088	0.133	0.155	0.082	0.086
	140 D	0.153	0.159	0.134	0.135	0.155	0.182	0.157	0.126
F_{45} (lb. per sq. in., based on 45- and 90-min. cures)	125 DR	106.8	106.9	91.4	91.5	99.1	100.2	149.3	154.2
	125 HR	112.7	108.2	94.4	97.1	104.4	103.3	156.2	146.4
	125 D	106.9	102.8	91.7	91.5	100.6	99.3	159.4	148.4
	140 D	101.1	100.0	91.0	92.0	100.0	102.0	136.5	134.3
k (min ⁻¹ , based on 45-min. cure)	125 DR	0.045	0.052	0.046	0.046	0.077	0.070	0.042	0.043
	125 HR	0.047	0.050	0.046	0.042	0.062	0.066	0.043	0.052
	125 D	0.052	0.054	0.054	0.046	0.058	0.066	0.040	0.042
	140 D	—	—	—	0.100	0.102	—	—	—

* Viscosity was increasing at 4 minutes. Minimum viscosity reported.

tion has the decided advantage of being below the point of crystallization of the rubber and thus avoids complications arising from this factor. In measuring the stress at 100 per cent elongation, there is one principal difference in the procedure used by the B.R.P.R.A. and the one in this study. The B.R.P.R.A. measures the force after a relaxation of the specimen at 100 per cent elongation for 1 minute. In this work, the grips of the Instron testing machine separate at the rate of 20 in. per min., and the force is measured when the 10-cm. bench marks on the specimen become 20 cm. apart. This difference causes a difference of absolute values, but it does not appreciably influence the relative characterization of the rubbers.

TABLE VII
STRAIN AT 100 PSI (PER CENT)

Treatment	Time of cure (min.)	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
		A	B	A	B	A	B	A	B
125 DR	12	312	287	388	422	166	157	160	151
	15	237	227	313	335	146	152	129	126
	20	183	167	245	247	139	137	103	102
	30	134	131	186	190	120	120	79	79
	45	114	109	153	159	108	109	68	67
	90	90	94	121	123	104	101	55	56
	180	89	90	108	112	100	99	54	55
125 HR	12	241	288	353	345	170	158	141	174
	15	195	227	286	283	150	152	120	143
	20	157	183	221	226	134	128	99	112
	30	128	148	178	177	117	113	79	85
	45	104	113	148	146	106	108	64	69
	90	90	92	116	113	95	98	54	56
	180	93	86	103	102	95	96	53	53
125 D	12	299	367	380	449	172	184	150	181
	15	234	288	319	347	157	165	122	144
	20	176	200	233	251	142	150	97	112
	30	131	151	182	187	127	130	78	91
	45	112	120	149	155	114	119	65	73
	90	93	98	119	123	106	107	53	58
	180	90	91	107	110	98	101	53	55
140 D	12	140	149	188	191	125	131	78	85
	15	124	135	175	172	119	125	71	79
	20	112	121	150	153	113	120	65	68
	30	102	107	131	136	107	114	59	61
	45	97	100	119	123	105	108	57	59
	90	100	106	126	123	102	103	65	65
	180	121	123	135	140	110	112	73	76

The individual values for stress at 100 per cent elongation are given in Table V. The average values for vulcanizates cured at 125° C are shown in Figure 4. The curves in this figure for the different rubbers are quite similar to those in Figure 3, with the exception that no pronounced reversion is noted for the vulcanizates cured 180 minutes. The same conclusions apply to the relative behavior of the rubbers.

The limiting modulus, F_{∞} , and the rate constant, k , of each compound, calculated according to the procedure given by Gee and Morrell⁴, are given in Table VI. The Mooney viscosities of the compounds are also given, since the value of this property is used to determine F_0 . Since the parameters are de-

pendent on the cures selected for calculation, the table lists values based on F_1 for both 15- and 45-minute cures and F_2 for 30- and 90-minute cures, respectively. The values of F_∞ calculated from the 15- and 30-minute cures are obviously much lower than the maximum values of stress at 100 per cent elongation given in Table V, except for vulcanizates cured at 140° C. Even the values of F_∞ calculated from the 45- and 90-minute cures are slightly lower than the stress at 100 per cent elongation for the 180-minute cures at 125° C in most cases. In essence, the values of F_∞ are approximately the values of F_2 used in the calculation and are virtually unaffected by the shape of the curve in Figure 4. The values of k are dependent on the cures selected for the calculation of F_∞ and k . These values indicate that at 125° C, pale crepe cures as fast as smoked

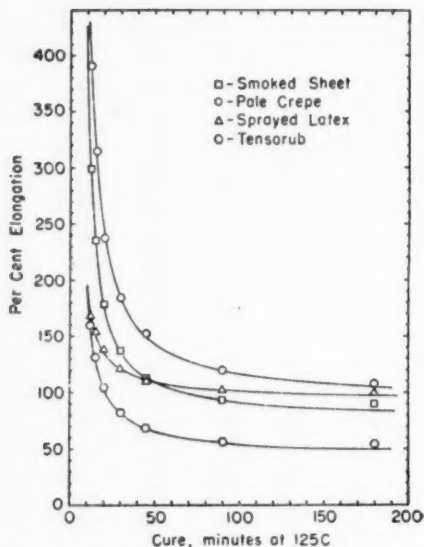


FIG. 5.—Strain at 100 lb. per sq. in. vs. time of cure.

sheet and Tensorub. This conclusion is not in accord with those derived from stress and elongation at failure.

STRAIN AT 100 LB. PER SQ. IN.

The N.B.S. strain test¹ was proposed in 1948 as a reliable method for evaluating the vulcanization characteristics of natural and synthetic rubber compounds. At that time, only limited strain data were available for natural rubbers. It was apparent, however, from these data that the load must be low, or anomalous results would be obtained because of crystallization. A load of 100 lb. per sq. in. was selected and has been used since then for all gum compounds. B.R.P.R.A. uses a load of 5 kg. per sq. cm. (about 70 lb. per sq. in.). Both loads should give results that lead to the same conclusions.

The individual values for strain at 100 lb. per sq. in. are given in Table VII. The average values for the compounds cured at 125° C are shown in Figure 5.

It is easily seen that the rubbers in order of decreasing rate are sprayed latex, Tensorub, smoked sheet, and pale crepe. This order is the same as that deduced from stress and elongation at failure data.

Unlike any other stress-strain property, strain values for different times of cure lie on a simple mathematical curve. This curve is a rectangular hyperbola with its axes displaced from the x - y axes. Three parameters uniquely define this curve. The three vulcanization parameters, t_0 , k , and E_∞ , calculated from the strain data for each compound in Table VII are given in Table VIII. In these calculations, the values for the 180-minute cure at 125° C and for both 90- and 180-minute cures at 140° C were omitted, since in most cases reversion has occurred. The time of incipient cure, t_0 , indicates sprayed latex to be the scorchiest, followed by Tensorub, pale crepe, and smoked sheet. The rate constant, k , indicates sprayed latex to be the fastest curing followed by Tensorub, smoked sheet, and pale crepe. The values of t_0 and k for cures at 140° C are not very reliable since there were no definite undercures.

TABLE VIII
VULCANIZATION PARAMETERS (N.B.S. STRAIN TEST)

Parameter	Treatment	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
		A	B	A	B	A	B	A	B
t_0 (min.)	125 DR	5.2	6.5	3.5	4.4	2.1	0.6	2.7	4.7
	125 HR	4.4	3.0	2.8	2.1	1.2	3.2	2.4	3.8
	125 D	6.1	6.3	4.3	5.7	1.3	1.2	3.1	3.1
	140 D	5.4	2.6	1.3	0.1	0.0	-7.5	5.5	7.3
$k \times 10^5$ (min.) ⁻¹	125 DR	61	84	40	40	143	122	99	119
	125 HR	78	51	42	39	109	155	104	92
	125 D	74	59	44	45	121	104	105	83
	140 D	293	166	97	91	253	144	586	605
E_∞ (per cent)	125 DR	71	80	92	94	95	92	43	46
	125 HR	75	69	89	84	85	91	43	43
	125 D	77	77	92	96	96	95	42	44
	140 D	88	86	95	99	93	95	53	54
t_p (min.)	125 DR	32.7	29.9	37.6	38.3	20.5	20.0	24.4	24.4
	125 HR	28.7	33.0	36.1	36.6	21.8	20.5	23.5	26.3
	125 D	31.1	34.5	36.8	38.0	20.9	22.3	24.1	26.7
	140 D	18.0	19.3	23.1	22.6	13.5	10.4	14.4	16.0

From t_0 and k , the time of preferred cure, t_p , can be determined by the method given by Schade². A factor must be empirically determined, however, since the factor 0.68 used by Schade applies to strain at 400 psi for GR-S tread-type compounds, and the selection of the factor depends on criteria other than strain data. As mentioned earlier, criteria that have been used heretofore for determining preferred cure are minimum time to reach maximum values of stress at failure, product of stress and elongation at failure, and stress at a selected elongation. These times as determined from Figures 1, 2, and 3 are not in agreement. Figure 2 yields the lowest values and Figure 3 the highest values. Since the values obtained from stress at failure in Figure 1 are intermediate, they have been arbitrarily used for determining the factor F in the equation: $t_p = t_0 + F \sqrt{1/k}$. By coincidence, the value for this factor is very near 0.68 used by Schade² for GR-S tread-type compounds. Until definite agreement is reached on the method of selecting the preferred time of cure, the

value 0.68 is used in this paper in order to avoid the introduction of another value for F in the literature at the present time. By its use, comparisons of Hevea rubbers can be made to determine the time interval required to reach the same state of cure which may or may not be near the optimum state of cure, depending on the criteria used to select the optimum state.

The values of t_p in Table VIII should be compared with these limitations in mind. They show that the time of preferred cure is least for sprayed latex,

TABLE IX
VULCANIZATION PARAMETERS FROM MOONEY VISCOSITY

	Treatment	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
		A	B	A	B	A	B	A	B
Minimum viscosity	125 DR	53.8	59.2	54.1	58.5	54.6	58.3	46.4	52.3
	125 HR	57.4	58.1	63.1	61.1	56.2	57.6	53.1	48.6
	125 D	58.5	56.8	63.0	59.1	53.4	52.0	50.9	47.4
	140 D	57.0	52.6	59.4	56.1	58.1	55.0	50.5	47.3
t_0 (min.)	125 DR	9.70	8.35	8.60	8.35	2.40	2.60	7.15	5.85
	125 HR	6.90	7.10	7.10	6.35	2.10	1.80	5.45	5.80
	125 D	9.35	9.30	8.80	7.40	2.90	2.80	6.60	6.35
	140 D	4.95	4.75	5.05	4.40	1.70	1.50	3.80	3.70
t_{30} (min.)	125 DR	1.80	1.65	2.40	2.35	1.35	1.30	1.35	1.25
	125 HR	1.90	2.20	2.30	2.35	1.20	1.20	1.25	1.50
	125 D	1.90	1.90	2.30	2.30	1.30	1.25	1.40	1.15
	140 D	1.15	1.15	1.35	1.40	0.90	0.80	0.95	0.70
$30/t_{30}$	125 DR	16.7	18.2	12.5	12.8	22.2	23.1	22.2	24.0
	125 HR	15.8	13.6	12.8	12.8	25.0	25.0	24.0	20.0
	125 D	15.8	15.8	13.0	13.0	23.1	24.0	21.4	26.1
	140 D	26.1	26.1	22.2	21.4	33.3	37.5	31.6	42.9
t_p (min.)	125 DR	36.7	33.1	44.6	43.6	22.6	22.1	27.4	24.6
	125 HR	35.4	40.1	41.6	41.6	20.1	19.8	24.2	28.3
	125 D	37.9	37.8	43.3	41.9	22.4	21.6	27.6	23.6
	140 D	22.2	22.0	25.3	25.4	15.2	13.5	18.0	14.2

followed by Tensorub, smoked sheet, and pale crepe; this is in agreement with the conclusions deduced from Figures 1, 2, and 3.

MOONEY VISCOSITY

Workers at The B. F. Goodrich Company⁵ have proposed a method for evaluating the vulcanization characteristics of rubbers by measuring the changes of the Mooney viscosity of the compound at vulcanizing temperatures. The method is an extension of ASTM Method D 1077-49 T¹⁰ in that a rate factor is determined as well as the time of incipient cure. The rate factor is the increase in the Mooney viscosity per minute after the time of incipient cure. It is determined by measuring the time required to increase 30 viscosity units above the viscosity at the time of incipient cure.

The time of incipient cure, t_0 , the time to increase 30 units after incipient cure, t_{30} , and the rate factor $30/t_{30}$, for each compound is given in Table IX. The values of t_0 indicate sprayed latex to be the scorchiest rubber, followed by Tensorub, pale crepe, and smoked sheet, which is the same order as that calculated from strain data. The values of t_0 in Table IX, however, are somewhat

higher than those in Table VIII. At least part of the difference is caused by the slower rate of heat transfer in the viscometer than in the press.

The values for the rate factor in Table IX indicate sprayed latex to be the fastest curing rubber, followed by Tensorub, smoked sheet, and pale crepe. This order is the same as that deduced from Figures 1, 2, and 3, and strain data.

Table IX also includes values of t_p corresponding to those calculated from strain data. They are calculated from the equation: $t_p = t_0 + 15t_{30}$. The factor 15 is the slope of the curve in Figure 6 which relates t_{30} to $(t_p - t_0)$ determined from strain data.

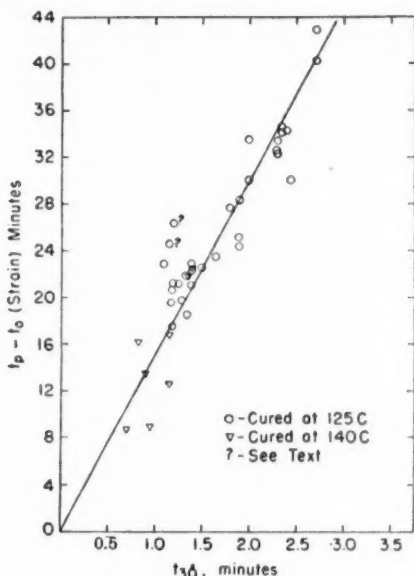


Fig. 6.—Relationship between measures of rate of cure determined from strain and Mooney viscosity tests.

PRECISION OF RESULTS

Thus far no mention has been made of the reproducibility of testing for each of the stress-strain properties included in this study. It was mentioned that the coefficient of variation for measurement of stress at 600 per cent elongation was about 3 per cent for the Instron machine and about 4 per cent for the Scott machine. These values apply, however, to variation among specimens from the same sheet of vulcanizate and do not indicate over-all testing variation, including variations in compounding and curing.

The reproducibility of measurements of stress and elongation at failure is known to be very poor. A cursory examination of the data obtained in this work confirms this well known fact. Consequently coefficients of variation have not been determined. An analysis of variance for the other properties shows that the reproducibility of testing is dependent on the state of cure. Consequently, the coefficients of variation were determined for the 15-, 30-, and 90-minute cures at 125° C. The values obtained for stress at 600 per cent

elongation, stress at 100 per cent elongation, and strain at 100 lb. per sq. in. are given in Table X. The values in the columns headed "relative" apply to vulcanizates that are compared to a reference rubber (compounded, cured, and tested along with the rubber under test) and are 1.4 times the within-day coefficient of variation for a single compound. The values in the columns headed "absolute" include day-to-day as well as within-day variations and apply to the absolute values measured.

It is seen that, as the state of cure increases, the coefficients of variation decrease. This fact is to be expected, since the undercures are sensitive to slight variations of the rate of cure, whereas overcures are relatively insensitive. The absolute values also tend to be slightly larger than the relative ones, a fact which indicates that, even in a laboratory that has controlled temperature and humidity conditions, the day-to-day variations in testing are slightly larger than the within-day variations. In laboratories where conditions are not controlled, the absolute values would be expected to be much larger than the relative values. Consequently, the use of a reference in evaluating rubbers results in an improvement of over-all reproducibility of test results. It has the added advantage of eliminating systematic variations among laboratories, which may be many times larger than the random variations of test.

TABLE X
COEFFICIENTS OF VARIATION FOR SINGLE VULCANIZATES
(IN PER CENT)

Property	Vulcanizate cured at 125° C					
	15 min.		30 min.		90 min.	
	Relative	Absolute	Relative	Absolute	Relative	Absolute
Stress at 600 per cent elongation	15.3	15.8	8.0	11.8	10.8	11.0
Stress at 100 per cent elongation	3.7	3.6	2.7	3.3	2.1	2.2
Strain at 100 lb. per sq. in.	6.7	7.7	5.5	5.5	2.1	2.8

The values in Table X are much smaller for stress at 100 per cent elongation than for the other two properties. This fact does not indicate that it is the best property for characterizing rubbers, since the merit or sensitivity of a test depends on both the range in values for different rubbers and the reproducibility of values for a single rubber. When the sensitivities are compared, it is observed that strain at 100 lb. per sq. in. is slightly better than stress at 100 per cent elongation, the ratio of sensitivities being about 1.25. By some changes of technique, the sensitivity of stress at 100 per cent elongation could undoubtedly be made equivalent to that of strain at 100 lb. per sq. in. The latter test, however, is easier to conduct.

Despite the large coefficient of variation for stress at 600 per cent elongation, its sensitivity is nearly equal to that of stress at 100 per cent elongation for short cures and about one-half the sensitivity at longer cures. To improve the sensitivity of this test would be difficult. Even if it were accomplished, the crystallization effects would make the test less desirable than stress at 100 per cent elongation or strain at 100 lb. per sq. in. for evaluating rubbers. This conclusion is substantiated by the observation that a single relationship exists

between stress at 100 per cent elongation and strain at 100 lb. per sq. in. similar to that reported by Blackwell¹¹. On the other hand, a separate relationship for each rubber is observed for stress at 600 per cent elongation and stress at 100 per cent elongation, apparently caused by differences in the amount of crystallization. Further, reversion is noted in values of stress at 600 per cent elongation sooner than in those of stress at 100 per cent elongation.

The sensitivity of stress-strain measurements cannot be readily compared with that of Mooney viscosity measurements. Since the time of incipient cure is measured directly in the Mooney viscometer, it is much more reproducible and sensitive than the values of t_0 calculated from strain measurements. A better index of comparison is to compare values of t_p calculated from strain data (Table VIII) with comparable values calculated from the time of incipient cure and the rate factor determined from changes in Mooney viscosity (Table IX). Such a comparison gives a standard deviation of 1.6 minutes for t_p (strain) and 1.76 minutes for t_p (viscosity).

TREATMENT OF COMPOUNDS

The results presented thus far show that a temperature of 140° C is too high for obtaining a definite undercure unless extremely short times of cure are used. Such short cures do not produce the necessary precision required for test purposes. Unless a definite undercure is obtained, a reliable measure of the rate of cure cannot be obtained from stress-strain data. For this reason this study has been predominantly on vulcanizates cured at 125° C.

The differences among the four rubbers in this study are so large compared to the differences resulting from treatment of compounds cured at 125° C that the effect of treatment has not been considered in comparisons of the rubbers. A more careful analysis, however, shows that there is an effect of humidity during storage before curing. The general effect of humidity is to reduce the time of incipient cure and to increase the ultimate stiffness of the vulcanizate. There is also a tendency toward more erratic results at high humidity, as might be expected, since absorption of moisture is not uniform throughout the compound.

In regard to the time of storage, a difference of 20 hours in storage times between treatments 125DR and 125D has no detectable influence on the results. Thus, a simple expedient for eliminating the humidity variable during storage is to store the compound after mixing in a small air-tight container until it is placed in the mold for curing or in the Mooney viscometer for testing.

DISCUSSION

In comparing the methods for the evaluation of Hevea rubber, the methods proposed by Thirion³ and Gee and Morrell⁴ lead to conclusions that are not in accord with the facts. In commenting on some of the data in Table V, Gee¹⁰ has suggested that the rubber be broken down to a viscosity below 40, since his method is based on the assumption that the uncured compound exhibits negligible elastic behavior. Two mixes of each rubber were, therefore, made, using a roll temperature of 50° instead of 70° C, and step 2 in the mixing procedure was increased to 5 minutes with the distance between rolls 0.055 inch. This procedure gave viscosities of the compound between 30 and 40 as shown in Table IX. The values of F_∞ calculated from the stress at 100 per cent elongation for the 15- and 30-minute cures are again appreciably lower than those calculated from 45- and 90-minute cure data. Further, the values of k are still

dependent on the cures selected to calculate F_{∞} and k . The values of k for the 45- and 90-minute cures indicate only slight differences among the rubbers, as can be seen in Table XI. At the shorter cures, sprayed latex is the only rubber having a value of k significantly different from the others.

A comparison of the values in Table XII with those in Tables VIII and IX shows that the increased breakdown causes an increase of the time of incipient

TABLE XI
MOONEY VISCOSITY, STRESS AT 100 PER CENT ELONGATION,
AND VULCANIZATION PARAMETERS (B.R.P.R.A.)
(Compounds mixed to viscosity below 40)

Cure at 125° C (min.)	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
	Day 9	Day 10	Day 9	Day 10	Day 9	Day 10	Day 9	Day 10
Viscosity ML-100° C (1 + 4 min.)								
—	39.4	37.3	39.9	37.0	32.3	30.2	36.2	33.2
F_0 (lb. per sq. in.)								
—	-7.11	-7.96	-6.83	-8.11	-10.66	-11.80	-8.53	-10.10
Stress at 100 per cent elongation (lb. per sq. in.)								
12	44	47	—	45	66	63	70	69
15	54	54	45	48	72	68	79	82
20	64	69	50	56	78	73	94	100
30	79	82	65	70	83	83	114	114
45	94	95	75	78	87	88	134	132
90	108	103	90	90	97	93	153	149
180	109	109	98	95	98	93	151	157
F_{∞} (lb. per sq. in.) (based on 15- and 30-min. cures)								
—	96.31	105.09	77.57	84.19	86.69	84.47	137.32	131.04
$k \times 10^3$, min ⁻¹ (based on 15- and 30-min. cures)								
12	57	55	—	71	136	119	64	68
15	60	53	63	62	134	111	61	70
20	58	57	56	59	133	99	61	76
30	60	53	63	62	134	111	61	70
45	84	54	78	60	—	—	84	—
90	—	44	—	—	—	—	—	—
F_{∞} (lb. per sq. in.) (based on 45- and 90-min. cures)								
—	110.25	103.67	93.37	91.94	98.14	93.26	155.92	151.31
$k \times 10^3$, Min ⁻¹ (based on 45- and 90-min. cures)								
12	48	56	—	63	102	104	54	56
15	49	54	49	55	95	95	51	56
20	47	58	42	51	84	82	49	57
30	44	55	42	51	66	78	46	49
45	44	57	38	44	51	67	45	47
90	44	57	38	44	51	67	45	47

cure and a decrease of the rate of cure. There is no essential difference in the relative behavior of the rubbers, except that the strain data for sprayed latex indicate a much slower rate of cure than the Mooney viscosity data do. The reason for this anomalous result is not apparent, since the correlation between cure rates determined from strain data and from Mooney viscosities are generally in agreement, as can be seen in Figure 6. The points indicated by question marks are the anomalous points for sprayed latex. The points in-

licated by triangles are for compounds cured at 140° C and are not so reliable for reasons previously mentioned.

The theory of Gee and Morrell⁴ indicates that the time of incipient cure or scorch time depends on the rate of cure and the molecular weight of the rubber. According to this hypothesis, the scorch time of smoked sheet would be less than that of pale crepe, since the rate of cure and ultimate modulus of smoked sheet are greater and the Mooney viscosities of the compounds of the two rubbers are nearly identical. However, both the strain and Mooney viscosity data show that the time of incipient cure for smoked sheet is greater than that for pale crepe. These results confirm other evidence obtained in studies of synthetic rubbers—that the time of incipient cure is an independent vulcanization parameter. In fact, the data of Gee and Morrell⁴ for different recipes confirm this conclusion.

TABLE XII

MOONEY VISCOSITY, STRAIN AT 100 PSI, AND VULCANIZATION PARAMETERS
(Compounds mixed to viscosity below 40 and stored overnight in closed container before curing)

	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
	Day 9	Day 10	Day 9	Day 10	Day 9	Day 10	Day 9	Day 10
Minimum viscosity	30.0	28.7	29.7	28.8	27.4	26.5	24.2	23.7
t_0 (min.)	11.3	10.0	11.3	9.3	3.8	4.1	7.4	7.0
t_{30} (min.)	2.00	2.00	2.90	2.70	1.15	1.20	1.40	1.40
$30/t_{30}$ (min ⁻¹)	15.0	15.0	10.3	11.1	26.1	25.0	21.4	21.4
t_p (min.)	41.3	40.0	54.8	49.8	21.0	22.1	28.4	28.0
Strain at 100 lb. per sq. in. in per cent (Cure at 125° C)								
12 min.	506	443	—	567	245	246	223	210
15 min.	375	325	567	458	210	214	168	163
20 min.	255	223	396	317	180	185	123	121
30 min.	167	152	257	220	150	156	88	87
45 min.	128	118	190	170	134	135	70	67
90 min.	96	93	136	126	118	119	56	54
180 min.	93	88	122	116	113	112	55	53
Strain parameters								
t_0 (min.)	6.7	7.0	6.6	5.0	2.9	1.8	6.1	5.6
$k \times 10^6$ (min. ⁻¹)	41	52	25	29	78	67	92	90
E_{∞} (per cent)	67	69	89	84	103	102	43	41
t_p (min.)	40.2	36.9	49.5	45.2	27.4	28.0	28.5	28.3

Further, Blackwell, Fletcher, and Gee⁹ claim that the stress at 100 per cent elongation is a function of the Mooney viscosity of the compounded rubber. A comparison of the data in Tables V and XI shows that the values for the shorter cures are higher in Table V than those in Table XI, but those for the longer cures are the same. These results are obviously the result of the differences in times of incipient cure and rate of cure. If they were dependent on the viscosity of the compound, as claimed by Blackwell, Fletcher, and Gee, all cures should be affected similarly. Thus it appears more likely that the effects of mastication on vulcanization are caused by organic acids formed during the process than by the decrease in molecular weight.

Apart from the rate of vulcanization, the most striking difference in properties of the rubbers is between Tensorub and the other three. The stress at failure for Tensorub in Figure 1 is 50 per cent higher, and in Figures 2, 3, 4, and 5, Tensorub is also conspicuously different from the other rubbers. Since the

Mooney viscosities of the Tensorub compounds are essentially the same as those of the other rubbers, the differences of properties cannot be ascribed to differences in the mean molecular weight of the compounded rubbers. Further, if the rubber molecules are joined by primary valences through a sulfur linkage, Tensorub should not differ so markedly from the other rubbers. The only apparent explanation is a difference of the amount or chemical composition of the nonrubber components that determine the chemical type of intermolecular forces in the vulcanizate. The material causing this effect does not appear to govern the rate of cure, since sprayed latex cures more rapidly than Tensorub and smoked sheet cures more slowly. In order to account for these results, the mechanism of vulcanization must be similar to that proposed by Stiehler and Wakelin¹².

Finally, it should be pointed out that both Thirion³ and Gee and Morrell⁴ base their evaluations of the vulcanization characteristics of Hevea rubbers on the assumption of a first-order reaction. It is believed that this assumption is responsible for the disagreement between the conclusions drawn from their methods of evaluation and the facts since, as pointed out by Roth and Stiehler¹, strain data indicate that vulcanization is a second-order reaction. This con-

TABLE XIII
TYPICAL OBSERVED AND CALCULATED STRAIN DATA
(Strain in per cent at 100 lb. per sq. in.)

Cure at 125° C (min.)	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
	Ob- served	Cal- culated	Ob- served	Cal- culated	Ob- served	Cal- culated	Ob- served	Cal- culated
12	312	311	388	389	166	166	160	153
15	237	238	313	311	146	149	129	126
20	183	182	245	245	139	134	103	102
30	134	137	186	187	120	120	79	81
45	114	112	153	153	108	111	68	67
90	90	90	121	121	104	103	55	55
180	89	80	108	106	100	99	54	49

clusion is substantiated by the poor agreement between calculated and observed values of stress data based on a first-order reaction and the excellent agreement that is obtained with strain data based on a second-order reaction. Table XIII shows typical calculated and observed strain values for the four rubbers used in this study. The validity of the conclusions deduced from strain data is substantiated by their agreement with conclusions deduced from Mooney viscosity data and from stress and elongation at failure.

It is apparent from this study that three parameters are required to characterize the vulcanization behavior of a rubber. Since sprayed latex, which is the fastest curing rubber, reverts less than some of the slower curing rubbers, reversion apparently is a secondary reaction independent of the vulcanization reaction. Consequently the vulcanization characteristics can be evaluated only under conditions where the reversion reaction is negligible.

SUMMARY

Comparisons have been made on four methods recently proposed for the evaluation of Hevea rubber. The following four rubbers were used: No. 1 ribbed smoked sheet, No. 1 pale crepe, sprayed latex, and Tensorub (a high-quality smoked sheet). These rubbers were selected because they represent a wide range in both rate of cure and ultimate modulus of the vulcanizate. It

was found that the methods proposed by Thirion and by Gee and Morrell, which are based on the assumption of a first-order reaction, lead to inferences that are not in accord with the experimental data. On the other hand, conclusions deduced from strain data, changes of Mooney viscosity during the initial vulcanization period, and measurements of stress and elongation at failure were found to be in essential agreement.

The results indicate that three parameters are necessary to characterize the vulcanization reaction. These parameters can be evaluated from strain data. Two of them can also be determined from changes in Mooney viscosity at the temperature of vulcanization.

For research purposes, it is desirable to determine the parameters from strain data. However, it is recommended that, for the technical classification of Hevea rubber, the time of incipient cure and rate of cure be determined from changes of Mooney viscosity, since this test is simpler and requires less time. In this test it is necessary that the temperature of the dies in the Mooney viscometer be controlled accurately and a recorder be used to permit a precise determination of the changes in viscosity with time. The ultimate stiffness or modulus can be approximated from the values obtained on a well-overcured vulcanizate in which reversion is negligible. For convenience of classification, the time of incipient cure and rate constant can be combined into a single parameter indicating the time required to reach a particular state of cure.

Finally, humidity conditions during storage before vulcanization have an effect on the vulcanization characteristics. In order to minimize day-to-day variations of the relative humidity, it is recommended that the compound be stored in a closed, air-tight container before vulcanization.

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DISCUSSION

MR. A. E. JUVE (B. F. Goodrich Research Center).—We have some lack of agreement between the papers by Mr. Veith and the one by Stiehler and Roth in one respect. Mr. Veith's paper concludes that the method of Gee and the

Mooney viscosity method are in very good agreement. Mr. Stiehler concludes that the Mooney viscometer method is very good and agrees with the strain data, but not with the data by Gee's method.

The essential difference between the two programs, I believe, is in the selection of the rubbers. Would Mr. Stiehler agree that the wide spread in the properties of the rubbers which he used is responsible for that lack of agreement?

MR. ROBERT D. STIEHLER (*author*).—I think that is correct. In the case of smoked sheet, there might be differences in the total amount of nonrubber components present, but in general these components will be present in the same relative proportion; however, with widely different rubbers prepared by widely different processes, these nonrubber components are probably present in different proportions as well as in different amounts. I think that this factor is causing the discrepancy in the results. There should be discrepancies in the conclusions deduced by Gee's method and by changes of Mooney viscosity, however, with some lots of smoked sheet, since the assumption of a first-order reaction is not valid.

MR. A. G. VEITH (B. F. Goodrich Research Center).—I think there are some features that should be elaborated upon at this time concerning the agreement between Mr. Stiehler's work, the work of Gee, and my work, which is allied to Gee's.

In making my application of Gee's work, reversion is neglected. It is not completely valid to do this, but a good approximation to the rate constant can be obtained if we neglect it. Also, the dependence of X or modulus on time is only first order over the initial period of cure, let us say from 0 to 40 minutes. After that it deviates.

Mr. Stiehler showed variation in the limiting modulus F_{∞} when the time values used for the calculation were varied. Since deviation from first-order kinetics is evident, F_{∞} will vary with the points on the curve which are selected to calculate it. The rate constant should be estimated during the initial period of vulcanization, since this is where first-order kinetics are most accurate in describing $F-t$ curves.

MR. STIEHLER.—We feel that the change of stress-strain properties does not indicate the kinetics of a first-order reaction, even during the initial period. There may be qualitative agreement in the results if first-order kinetics are restricted to the early cures.

MR. GEOFFREY GEE (British Rubber Producers' Research Association) (*by letter*).—Although this paper represents a very welcome effort to compare methods which have recently been suggested for the evaluation of vulcanization characteristics of natural rubbers, it is open to question how well the experiments were designed for this purpose. Certainly, in the case of the British Rubber Producers' Research Association method, both the design of the experiments and the discussion of results are quite out of harmony with the original objective for which the method was designed.

It must be emphasized here that the objective of the B.R.P.R.A. work was not the fitting of experimental data obtained by some arbitrary experimental procedure, but the much more ambitious one of making and interpreting measurements which have definite physical meaning in terms of cross-linking.

The first essential is a quantitative measure of cross-linking, and it was shown that stress at 100 per cent elongation could be so used with certain limitations. These limitations arise primarily from two sources: (1) the finite

molecular weight of the rubber in the uncured compound, and (2) the fact that even unvulcanized rubber gives a finite modulus in any practical modulus test. To meet the first of these difficulties, a correction factor was devised in terms of the Mooney viscosity of the compound, but it was perhaps not made sufficiently clear that this is unreliable at very high or very low Mooney values; the range 30 to 45 is preferred. The second limitation furnishes a further reason for avoiding compounds mixed to a high viscosity; it too implies the need to make modulus measurements under equilibrium conditions. As a practical approach to this, it is recommended that 1 minute be allowed for relaxation after loading before a reading is taken. Even when this was done, it was observed and reported that modulus measurements lower than 4 kg. per cm. (56 lb. per sq. in.) systematically overestimate cross-linking. It is believed that modulus determination at 100 per cent elongation, carried out as recommended, furnishes a quantitative measure of the state of cure which is applicable over a fair range of the curing curve (excluding fairly gross undercures).

The next step in the B.R.P.R.A. method is the empirical observation that an equation having the same mathematical form as a first-order chemical reaction could be applied, in a number of cases, to describe the development of cure so assessed. It was shown that this method, which is frankly empirical, is not of universal application, but the data available at the time supported the view that it could be applied to a normal sample of smoked sheet, vulcanized in one of several mixes, which included A.C.S. No. 1. Where applicable, the method has the attractive feature of assessing rate of cure in terms of a single constant, having dimensions time^{-1} . Together with the ultimate modulus, F_{∞} , this gives a complete description of the equilibrium elastic properties of the vulcanizate at any time of cure.

It is clear that the work of Stiehler and Roth was not planned to take account of the requirements of this method. The initial data for stress at 100 per cent elongation, recorded in Table V, were obtained on compounds mixed to Mooney viscosities in the neighborhood of 70. As mentioned in the paper, these were subsequently repeated at lower viscosities and recorded in Table XI. Even these results are subject to criticism on the grounds that measurements were made during continuous elongation, instead of allowing a period for relaxation. In a private communication, Stiehler has now reported that relaxation for 1 minute does indeed reduce the observed modulus by 2 to 8 lb. per sq. in., the reduction in general being greatest for the shortest times of cure. This final, and hitherto unpublished, set of results is the only one which really aims to meet the conditions of measurement implicit in the B.R.P.R.A. method and, therefore, the only one to which this method can properly be applied.

Given data obtained with due regard to the requirements of the method, the next question to be considered is the use to be made of them. The choice is between (1) using them to test the method and (2) assuming the method in order to compare rubbers. Stiehler and Roth have in the main attempted the former, but their discussion is confused by the unsuitable nature of the published data. Their criticisms appear to follow two main lines: (1) the value found for F_{∞} depends on which two of a series of cures is used in its estimation; (2) with any fixed value of F_{∞} , the value of k varies systematically with the length of cure from which it is calculated. These two observations are rightly taken by Stiehler and Roth to prove that their experimental data do not conform accurately to a theoretical curve of the form of a first-order equation.

It is believed that the reply to this criticism is contained in the outline of the method presented at the beginning of this note. The method does not set

out to measure modulus; it aims to measure cross-linking and, to this end, makes the best use it can of modulus data, chosen in preference to other data largely for their ready availability. The failings noted by Stiehler and Roth are just those to be expected if modulus data overestimate cross-linking by an amount which increases progressively as the cure is shortened, behavior which is known to occur. It is indeed difficult, if not impossible, to formulate an adequate experimental test of the method without supplementing the modulus data by swelling measurements to enable the cross-linking of undercured compounds to be properly estimated. Gee and Morrell found that, when this was done, their first-order equation fitted very well. It is reluctantly suggested that the data of Stiehler and Roth do not constitute a wholly satisfactory test of the method, and it is significant that the fit of the equation is notably better with the new data than with any of the old. Before introducing an arbitrary time zero (as is done in the strain hyperbola method), it is surely desirable to have much better evidence for its necessity than is presented here.

Although the data are thus disappointing as a source of a critical test of the B.R.P.R.A. method, it is believed that interesting and valid comparisons can be made by applying the method to the results obtained for the four rubbers, for which purpose the final data are amply adequate. To do this, F_{∞} could conveniently be taken as equal to the 180-minute reading; extrapolation from the 45- and 90- or 90- and 180-minute readings makes no appreciable difference, especially as regards comparisons between rubbers. For reasons set out in the original description of the method, the best time of cure to use in calculating the rate constant is about 30 minutes. Taking this value, with F_{∞} extrapolated from the 45- and 90-minute readings, Stiehler and Roth obtain the following values from their new data:

	Smoked sheet	Pale crepe	Sprayed latex	Tensorub
F_{∞} (lb. per sq. in.)	108	91	92	147
$F_{\infty} - F_0$ (lb. per sq. in.)	115	99	104	156
$1000 k$ (min^{-1})	44	45	[74]	48

The rate constant for sprayed latex is bracketed because the value obtained is so highly dependent on the time of cure selected as to make it clear that the method is inapplicable to this rubber. The "constant" is very high at short cures, an indication that the rubber initially cures very rapidly and is evidently highly scorchy. On this evidence, this rubber behaves quite differently from a normal smoked sheet, and would be altogether unacceptable as a standard rubber (for which it has been proposed). The remaining three rubbers all appear to have normal cure curves, and there is no evidence of any significant differences among their rates of cure. On the other hand, their maximum moduli (best evaluated by $F_{\infty} - F_0$) vary widely, Tensorub being outstanding in its very high modulus.

It is interesting to compare the results of this analysis with the conclusions drawn by Stiehler and Roth. On the basis of time to optimum tensile strength, the order found for rate of cure was sprayed latex > Tensorub > smoked sheet > pale crepe. This order is reproduced approximately by the N.B.S. strain test, by Schade's modification of it, and also by Juve's Mooney scorch method. All three, however, place Tensorub close to sprayed latex (with an occasional reversal), with the other pair close together but much slower. Thirion's method is the only one which agrees with that of B.R.P.R.A. in grouping Tensorub with smoked sheet and crepe for rate of cure. It is suggested that the reason the

other methods represent Tensorub as fast curing is that they involve a confusion between high modulus and rapid cure, a confusion which is only resolved by use of a rate constant defined in line with a recognized form of rate equation.

Finally, a comment should be made on the method of assessing the relative values of the different lines of approach. Stiehler and Roth appear to argue that because the (reciprocal) time to reach maximum tensile strength is the oldest method of assessing rate of cure, any method which fails to reproduce the same order is automatically unacceptable. This attitude is far removed from that taken by this Association in presenting its group of papers on the quantitative characterization of cure. It is strongly maintained that the measurement of rate of cure—that is, rate of build-up of the cross-linked structure—is a legitimate end in itself, irrespective of what use might be made of it. Such a quantity should be sharply distinguished from purely technical concepts such as "optimum cure", which may well depend on the use to be made of the vulcanizate.

Rate of cure (in a given compound, at a defined temperature) is regarded as a fundamental property of a rubber, with ultimate attainable modulus ($F_{\infty} - F_0$) as a second such property. In many cases (for example, in a set of smoked-sheet samples), the two may be closely correlated, but the data under discussion show the correlation to be limited in scope. The B.R.P.R.A. method of measuring rate of cure is admittedly neither perfect in detail nor universal in application. Within its limits, however, it appears capable of wide usefulness, and it is hoped that it will receive an adequate trial. Scorch measurements are considered less fundamental, depending on initial Mooney level and on F_{∞} as well as on rate of cure. Nonetheless, their simplicity commends them and, in association with other data, they appear capable of giving useful information. The further development of Juve's work will be watched with great interest.

MR. STIEHLER AND MR. F. L. ROTH (*authors*).—Mr. Gee stresses the differences in the manner of approach and objective of the B.R.P.R.A. and N.B.S. studies. It seems to us that the objective of both studies is to unravel the mechanism of the vulcanization reaction and to characterize the vulcanization behavior of rubber in quantitative terms. In this connection we should like to emphasize that the success of any theory is measured by its ability to account for all the facts and that it is immaterial whether the theory is deduced from experimental observations or from theoretical considerations. Further, Mr. Gee is apparently of the opinion that time of incipient cure (scorch time) originated with the strain test as an arbitrary parameter used in the empirical fit of data to a curve. We should like to point out that Weaver reported on the use of the Mooney viscometer to measure this parameter in 1940¹. Prior to this publication, it was recognized that some acids and accelerators markedly increased the scorch time independently of their effect on rate of cure. Thus, the independence of scorch time as a vulcanization parameter was established long before the strain test was developed. In fact, Mr. Gee noted in his published data that the scorch time of his compound TA 57 could not be explained by his theory. Therefore, to assume that scorch time is not an independent parameter in the case of the A.C.S. No. 1 recipe is unjustified and contradicted by the data presented in our paper.

Mr. Gee has prescribed very limited conditions under which his method of characterizing rubbers would be applicable. In obtaining our data, we did not comply with the condition which allows a relaxation of 1 minute before measuring the stress at 100 per cent elongation. This condition was not used since previous studies of strain measurements, made after times of creep ranging

from less than 10 seconds to 10 minutes or more indicated that the time of creep is not critical (if kept constant) in comparing the vulcanization characteristics of rubbers by the strain test. Nevertheless, at Mr. Gee's suggestion, tests were made subsequent to the presentation of the paper which complied in every respect to the conditions set forth by him. The results are given in the accompanying Table XIV. It is seen that the values of F_{∞} are substantially the same whether stress at 100 per cent elongation is measured in the manner

TABLE XIV
EFFECT OF RELAXATION OF ONE MINUTE DURING TEST ON
VULCANIZATION PARAMETERS (B.R.P.R.A.)

Cure at 125° C (min.)	Smoked sheet		Pale crepe		Sprayed latex		Tensorub	
	Original	Relaxed	Original	Relaxed	Original	Relaxed	Original	Relaxed
	F_0 , psi							
	-7.68	-7.68	-8.25	-8.25	-11.52	-11.52	-9.95	-9.95
	Stress at 100 per cent elongation (lb. per sq. in.)							
12	48	41	42	34	67	63	71	63
15	56	50	50	43	72	67	80	73
20	68	63	57	53	77	74	95	88
30	82	77	67	65	84	81	114	109
45	93	90	78	74	89	87	129	123
90	108	105	90	88	95	92	149	143
180	110	107	94	92	97	95	151	144
	F_{∞} (lb. per sq. in.) (based on 15- and 30-min. cures)							
	99.94	100.76	74.01	81.55	86.01	84.04	134.66	136.60
	$k \times 10^3$, min ⁻¹ (based on 15- and 30-min. cures)							
12	61	50	69	53	136	126	68	57
15	60	51	82	56	129	115	65	57
20	61	53	79	57	119	113	65	55
30	60	51	82	56	129	115	65	56
45	61	51	—	55	—	—	72	53
90	—	—	—	—	—	—	—	—
180	—	—	—	—	—	—	—	—
	F_{∞} , psi (based on 45- and 90-min. cures)							
	110.62	107.72	91.94	90.87	95.38	92.27	152.36	146.64
	$k \times 10^3$, min ⁻¹ (based on 45- and 90-min. cures)							
12	53	46	58	46	110	105	58	52
15	52	46	58	48	101	94	54	50
20	51	47	53	48	88	87	52	49
30	47	44	47	45	75	74	48	48
45	42	42	44	39	63	66	43	42
90	42	42	44	39	63	66	42	42
180	—	28	—	—	—	—	27	23

described in the paper or after 1 minute relaxation. The values of k tend to be smaller after relaxation, but the relative differences between rubbers are essentially the same. Also, the values of k for sprayed latex and Tensorub decrease most with increasing time of cure, even though they should be the most constant, according to the criteria of Mr. Gee. Thus, the conclusions in the paper are not affected by this change in method of measurement.

We cannot follow the reasoning of Mr. Gee which implies that the relative rates of cure given by his method and Thirion's are correct and those by al-

other methods are confused with modulus. We do not understand how modulus enters the determination of rate of cure by changes in Mooney viscosity. The four rubbers start with approximately the same viscosity and increase in viscosity the same amount. Yet this method shows Tensorub to be almost as fast curing as sprayed latex.

In summary, we feel that the evidence presented in the paper is sufficient to show that the assumption of a first-order reaction for vulcanization is not valid and that any method based on such an assumption should not be used for the classification of rubber.

MR. R. G. NEWTON (International Rubber Research Board)². (*by letter*).—In the opening words of their paper, Stiehler and Roth suggest that technically classified natural rubber is handicapped by an inadequacy in the test for the vulcanization characteristic (color coding). This contributor contends that this is not so and, as many will not know the reasons for adopting the present test, a brief account will be given of the developments during the last three years.

The original scheme, proposed by the French Delegation to the 1949 Meeting of the International Rubber Study Group, used a single modulus measurement (at 600 per cent elongation of the internal circumference of a Schopper ring) at an undercure (40 minutes at 127° C) in the A.C.S. No. 1 mix to characterize the rate of cure, and used the colors red, yellow, and blue to designate respectively slow- medium- and fast-vulcanizing rubbers³. In doing this, the sponsors of the scheme deliberately adopted substantially the same test procedure and terminology recommended by the American Chemical Society⁴.

It was soon realized that, if widely different rubbers were chosen, examples could be found which possessed the same time rate of cure but differed in modulus at the chosen cure or, conversely, gave the same result for the standard modulus test but clearly differed in rate of cure. This concept was pointed out in a paper read to the Rubber Division of the A.C.S. in Atlantic City on September 21, 1949⁵. It was thus evident that the original recommendations of the American Chemical Society were inadequate, and those⁶ who were charged with the scientific development of T. C. rubber sought a better test for the rate of vulcanization of natural rubber. Unfortunately there was no suitable test readily available, and work was instituted to develop such a test⁷.

On the other hand, it was equally evident that the T.C. scheme could not stand still and the existing test, or one like it, would have to be used. As far as public statements about the color classification of T.C. rubber were concerned, however, all references to rate of cure were dropped, and the three colors—red, yellow, and blue—were referred to as characterizing only low- medium-, and high-modulus rubbers⁸.

Extensive surveys of natural rubber were already in hand, and it soon became evident that, when attention was restricted to one kind of rubber only, the maximum modulus developed in the A.C.S. No. 1 mix was highly correlated with the rate of cure, at least when measured by the time required to develop that maximum modulus⁹. It was also clear that the existing test, made at a relative undercure, measured a mixture of the modulus characteristic and the rate of cure characteristic and that, as no agreed method was available for determining the "true" rate of cure, and as the color-coding of T.C. rubber referred to the modulus level, it would be better to measure only the modulus rather than the "mixture" referred to above.

This modulus characteristic would clearly be measured better by determining the maximum modulus, or at least by prolonging the cure until the plateau

part of the curve was reached. Work along these lines produced the interesting result that the ability of the test to discriminate between rubbers was enhanced by curing to about maximum modulus. This was an additional reason for attaining the plateau part of the curve and, as the A.C.S. No. 1 mix required vulcanizing for some 160 minutes at 127° C to do this, it was preferable to increase the vulcanizing temperature to 140° C, thus shortening the curing time to 40 minutes.

It was for this reason that, at the third meeting of I.S.O. Technical Committee 45, held at Akron in October, 1950, the Secretariat Delegation proposed that the vulcanizing characteristic of T.C. rubber should be a modulus test after vulcanizing for 40 minutes at 140° C. This test was accepted by all delegations except the French, but the French delegation subsequently accepted the test, and it was thereupon adopted by the International Rubber Research Board as from January 1, 1951.

The I.R.R.B. is aware that a test for rate of cure might be preferable to the present modulus test, but Stiehler and Roth's paper makes it clear that no test as yet commands general acceptance. If a simple rate of cure test gains widespread favor, as it seems that the Mooney scorch test may do¹⁰ the I.R.R.B. will be ready to adopt it.

Another matter on which this contributor would challenge Stiehler and Roth is their assertion that any proposed rate of cure test "must agree, qualitatively at least, with the stress and elongation at failure in classifying rubbers in order to be generally accepted". Not only does this method of characterizing cure already appear to be outmoded, but there is considerable doubt as to whether the assertion can be made, as the authors do, that the curing rates are: fastest, sprayed latex, Tensorub, smoked sheet, pale crepe, slowest. The data in Tables II and III for cures at 125° C were presented to several competent British rubber technologists without disclosing the nature of the four rubbers. The results were quite enlightening, especially as regards the Tensorub, which was placed, by one technologist or another, in every possible position from fastest to slowest! There was much more agreement about the sprayed latex, which was placed fastest or, rather exceptionally, second to Tensorub. Apart from the Tensorub, pale crepe seemed to give the most trouble, being placed almost equally often as second, third, or slowest. The smoked sheet was generally placed either second or third or (exceptionally) slowest. It would thus seem that Stiehler and Roth are on insecure ground when they claim the methods of Thirion¹¹ and Gee and Morrell¹² are "not in accord with the facts".

Towards the end of their paper, Stiehler and Roth refer to the excellent agreement between calculated and observed values of strain data, based on the strain hyperbola as shown in Table XIII.

This contributor believes that some features of the strain hyperbola are not generally understood, and it is hoped that the following observations will help to clarify the position.

1. None of the three parameters of the strain hyperbola can be determined directly; hence, the hyperbola can be fitted perfectly to any three points, provided only that the strain decreases with increasing time, t , and the three points are not in a straight line. This is a simple fact of algebra and has nothing to do with the properties of rubber; thus when three cures are used, the calculated points will always agree perfectly with the observed points, even though the latter may contain gross errors, or falsifications due to mistakes in copying, or may even be entirely fictitious,

TABLE XV

Time of cure (min.)	Strain at 100 lb. per sq. in. (per cent)		$k(t - t_0) / (E - E_\infty)^a$
	Observed	Calculated ^a	
12	166	166	1.000
15	146	149	0.946
20	139	134	1.147
30	120	120	1.000
45	108	112	0.749
90	104	104	1.000
180	100	100	0.912

^a $t_0 = 2.91$, $E_\infty = 96.78$, $k = 158.9 \times 10^{-5}$.

2. Thus, if five cures are given (and strain decreases with increasing time), it is always possible to fit three points exactly, and we are interested in agreement between calculated and observed points only in the case of the remaining two points. Moreover, it is somewhat misleading to compare calculated and observed strain values, because the constant E_∞ is usually a substantial part of the strain, and variations of the relevant $(E - E_\infty)$ are, therefore, obscured. In judging whether the strain hyperbola has been successful in describing the data, attention should be given to an alternative criterion which involves only the three operative portions, that is, $k(t - t_0) / (E - E_\infty)$, which should equal unity in each case. The accompanying Table XV shows the values of the different quantities for the seven cures in the case of sprayed latex, treatment 125DR, batch A. The three "fitted" cures are 12, 30, and 90 minutes and they can, therefore, be ignored; in the case of the other four cures, there appears to be a good agreement between the observed and calculated strain values, but it is evident from the value of $k(t - t_0) / (E - E_\infty)$ that on the basis of this criterion the hyperbola does not "fit" the 20- and 45-minute cures at all well.

3. Even the amount of agreement which is shown in Table XV is obtained only because the fixed cures are spaced among the others, and attempts to fit a hyperbola, using only the first three points or the last three points, result in gross misfits at the other end of the curve.

4. The paper under discussion is mainly concerned with evaluating the rates of cure of the rubbers, and the inadequacy of the strain hyperbola, compared with Gee's equation based on an assumed first-order reaction, can be shown by estimating the respective values of k as obtained from the different cures.

The crucial test of the strain hyperbola will be to examine a normal rubber rather than the sprayed latex used for Table XV, and to use the most advantageous method of plotting—that is, fitting the hyperbolas to pass through the 12- and 90-minute cures and then calculating a separate value of k for each of

TABLE XVI
REPRODUCIBILITY OF THE VALUES OF k

Cure (min.)	Stiehler and Roth's $k \times 10^5$	Gee's $k \times 10^5$
12	—	48
15	63	49
20	59	47
30	67	44
45	54	44
90	—	44

the intermediate cures. This has been done in Table XVI for smoked sheet, treatment 125DR, batch A (using the data in Table VII), and the four values of Stiehler's k are seen to vary between 54 and 67 (the range of 21 per cent of the mean value), whereas the six values of Gee's k (taken from Stiehler and Roth's Table I) vary between 44 and 49, or only about 10 per cent of the mean value.

This analysis would suggest, contrary to the arguments advanced by Stiehler and Roth, that Gee's treatment is more valid than theirs.

Finally, a comment could be made on the sprayed latex, which Mr. McCollm¹³ suggests would be suitable for use as a standard rubber because it has been prepared in a uniform manner. In view of the data presented by Stiehler and Roth, this contributor regards the very fast cure, the tendency to scorch, and the general shape of the plots relating various characteristics with time of cure, as being so exceptional as to render the material unsuitable as a rubber for standardizing normal mixing and curing operations.

MESSRS. STIEHLER AND ROTH.—We concur with Mr. Newton that the present classification of natural rubber is based essentially on the limiting or maximum modulus and not on rate of cure. In the United States, uniformity of rate of cure is considered of prime importance, and any classification scheme that does not include this characteristic is inadequate and handicapped. Mr. Newton implies that rate of cure has been omitted from the present classification scheme because (a) a suitable test is not available and (b) the rate of cure of smoked sheet is related to the maximum modulus. In regard to the first point, we feel that the Mooney viscosity method published in 1947 and the strain test published in 1948 are both satisfactory for this purpose. If the second point were true, a cure of 40 minutes at 127° C should be as reliable as any other one for characterizing smoked sheet, and there would be no need of going to a cure of 40 minutes at 140° C. The apparent acceptance of this latter cure by the United States delegation at the third meeting of I.S.O. Technical Committee 45 in Akron, Ohio, during October, 1950, is the result of a misunderstanding. At that time, studies of other recipes were in progress, and the United States delegation mentioned that ASTM Committee D-11 was developing standard recipes using benzothiazolyl disulfide (instead of mercapto-benzothiazole) and that this required a curing temperature of 140° C. It was also mentioned that certain wild rubbers require this higher curing temperature, even with the A.C.S. No. 2 recipe. However, there was no intention on the part of the United States to change the temperature of vulcanization recommended by the A.C.S. Crude Rubber Committee for the evaluation of plantation rubber using the A.C.S. No. 1 recipe. The U. S. delegation clarified its position on this point at the fourth meeting of I.S.O. Technical Committee 45 in Oxford during October, 1951.

In regard to the characterization of rubber from stress-strain properties, in particular stress and elongation at failure, we point out in our paper better methods of evaluation. Nonetheless, we are unaware of any evidence which shows that these properties give misleading information concerning the state of cure of rubber. Insofar as the relative rates of cure of the four rubbers are concerned, the reader can examine the data in Tables II and III and in Figures 1, 2, and 3, and form his own conclusions.

Mr. Newton also comments on the strain hyperbola. His comment on fitting an hyperbola to three points does not seem pertinent to our work, in which the hyperbolas were fitted to five or six points instead of three. Further,

we do not subscribe to calculating parameters from three points, as was done in Mr. Newton's Tables XV and XVI. It is axiomatic that a curve, linear or otherwise, should be determined by the method of least squares. Since an hyperbola is difficult to determine in this manner, we calculate the strain parameters by a method which employs all cures (excepting those where reversion occurs) and approximates a least square fit. If this method of calculation is used, the values in the last column of Table XV are in better agreement. It should be noted that the case illustrated in Table XV is an extreme one. Much less variation is observed with most of the other mixes either of sprayed latex or of the other rubbers. The maximum variation in the products that are observed are caused by an error of about 3 per cent in the strain values, which is well within the precision of reproducing vulcanizates for test. The comparison of the reproducibility of the values of k in Table XVI is misleading. Different values of t_0 and E_∞ are used for each cure to calculate the k values from strain data, whereas the same value of F_∞ is used for the k values from stress at 100 per cent elongation. Obviously, the same t_0 and E_∞ should be used for all cures. If the values for these parameters given in the paper are used, the values of $k \times 10^5$ for the six cures are 61, 61, 60, 64, 58, and 62, respectively. Although the spread in these values for k is about the same as those given in the last column of Table XVI, it should be noted that they show no trend. Our criticism of the B.R.P.R.A. method is based on the systematic trend in the values of F_∞ and k and not on the variation caused by errors of test. Incidentally, it should be pointed out that the case for smoked sheet illustrated in Table VXI is the most favorable on for the B.R.P.R.A. method.

The last comment of Mr. Newton refers to the use of sprayed latex for a standard rubber. We concur with him, and point out in our discussion of Mr. McCollm's paper that the rate of cure of the sample used in these investigations is much too fast for this purpose. Mr. McCollm indicates that a slower curing lot of sprayed latex can be prepared.

MR. VEITH.—This paper makes it necessary to mention a not too evident yet important feature of Gee's theoretical development of rate of cure. It is simply that the cure rate constant k evaluates rate of cure on a basis that requires the incorporation of the limiting or infinite time of cure modulus as a reference point.

The following example will indicate this. Suppose there are two mixes A and B which have limiting moduli (that is, F_∞) of 5 and 10 kg. per sq. cm., respectively. Assume that, after 20 minutes of cure, the modulus of A is 3 and that of B is 6 kg. per sq. cm. It might be said, if the modulus at 20 minutes of cure is used as a criterion, that B is curing faster than A. However, it is easily seen, if plots of $\ln(F_\infty - F)$ vs. t are made, that the value of k is identical for the two mixes (assuming that $F = 0$ at zero time). Thus it is possible for mixes having vastly different moduli at any time t to have the same rate of cure when k is used as a measure of cure rate. Figure 4 of this paper gives the 100 per cent modulus-time curves for the four rubbers. As mentioned by the authors, the order of increasing modulus at, let us say, 30 minutes of cure is pale crepe, smoke sheet, sprayed latex, and Tensorub. Table V shows that, generally, the value of k for the first three rubbers increases in the order: pale crepe, smoked sheet, and sprayed latex, while the value for Tensorub is slightly lower than that for pale crepe. With the exception of Tensorub this is the same order as shown in Figure 4. Both these methods place three out of four of the rubbers in the same order, although this is not required for a compatibility between the

two methods. (The low value of k for Tensorub may be due in large part to the very high limiting modulus.)

The customary and empirical method whereby the modulus at a given time of cure is used as a measure of cure rate may be termed the zero reference method. At a specified time, cure rate is proportional to the modulus increase above a fixed level, assumed to be zero. In any future comparison between these two methods, the detailed nature of assessing cure rate by the rate constant k should be kept in mind.

MESSRS. STIEHLER AND ROTH.—We concur with Mr. Veith that rate of cure is independent of the limiting modulus. We might also add that scorch time is another independent parameter. Although we have shown correlation between the scorch time calculated from strain data with that determined from changes of Mooney viscosity at vulcanizing temperatures, this parameter is

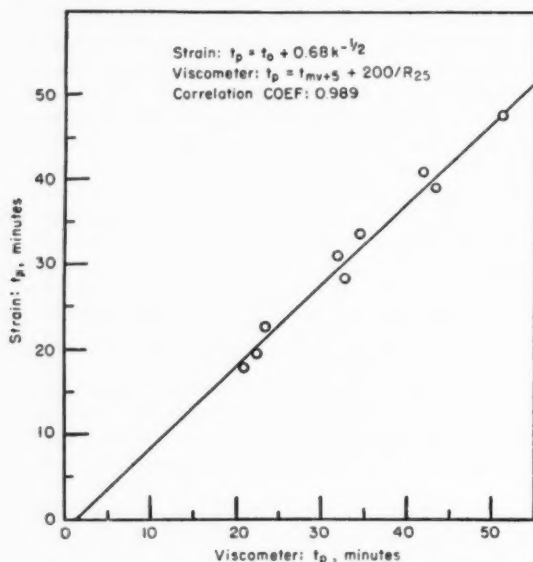


Fig. 7.—Correlation of values of t_p determined from strain and viscometer tests (data of A. G. Veith).

much more precisely determined by the Mooney viscometer. The poor correlation between the scorch times determined by the two methods that was mentioned in the paper by Mr. Veith can be attributed to the uncertainty in the value calculated from strain data for a single mix. If values of t_p are calculated from the strain and Mooney viscosity data of Mr. Veith, good correlation is obtained, as can be seen in the accompanying Figure 7.

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STRUCTURE AND PROPERTIES OF LOADED RUBBER MIXTURES. VIII. TENSILE STRENGTH OF LOADED RUBBER MIXTURES PREPARED DIRECTLY FROM LATEX *

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The work of Dogadkin and Uzina¹ indicated the possibility of reinforcing films of natural and synthetic latexes by the addition of highly dispersed fillers, as of the kaolin and bentonite clay types. They also established that the strength of films of natural latex mixtures containing bentonite clay as a function of the degree of loading is represented by a curve with a minimum at 5-15 parts by weight and a maximum at 50 parts by weight of filler. The density also changes in proportion to loading. On the basis of these studies the authors concluded that the strength of latex films depends on the nature of their structure. A linear relation between tensile strength and density was established in the region up to the loading optimum.

The present paper is a continuation of the above mentioned work on the structure and properties of loaded latex mixtures, and considers problems connected with the structure of loaded latex films and the properties of the bond at the rubber-filler interface in relation to the nature of the substances adsorbed on the latex globules.

THE EXPERIMENTAL METHOD

Latex mixtures of natural latex (Revertex) and synthetic latex (Igetex S-3), loaded with bentonite clay and channel carbon black, were studied. The colloid chemical characteristics of the latexes and fillers are shown in Tables 1 and 2.

TABLE 1
COLLOID-CHEMICAL CHARACTERISTICS OF LATEXES
(Concentration 30 per cent)

Type of latex	Relative viscosity	pH	Surface tension (dynes per cm.)	Angle
Natural	2.36	9.6	35.0	32°45'
Synthetic	2.20	9.9	35.5	38°2'

The mixtures were prepared in three different ways: (1) all the compounding ingredients of the latex mixture (fillers, accelerators, and sulfur) were added in dispersed form to the latex protected by ammonium caseinate, and the mixture was either coagulated or dried; (2) the fillers were added in dispersed form to the latex, the resulting mixture was then either dried or coagulated, and the

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Kolloidnyi Zhurnal* (Colloid Journal), Vol. 14, No. 3, pages 197-203 (1952).

TABLE 2
CHARACTERISTICS OF FILLERS

Type of filler	Size of particle	Specific gravity	Moisture content (%)	Ash content (%)	Apparent volume in dry state
Channel carbon black	~30 m μ	1.75	3.33	0.03	4.5
Bentonite clay	~ 2 μ	1.92	—	—	—

remaining ingredients (sulfur, accelerator) were added to the latex mixture on a mill; (3) all the ingredients of the latex mixture were added to the dried or coagulated latex rubber on a mill.

The natural-latex mixtures were coagulated by acetic acid; the synthetic latex mixtures by a saturated solution of aluminum chloride.

The composition of the latex mixtures is given in Table 3.

TABLE 3
COMPOSITION OF LATEX MIXTURES

Composition of mixture	I 5-15 parts by weight of filler in latex-rubber		II 15-25 parts by weight of filler in latex-rubber		III 25-60 parts by weight of filler in latex-rubber	
	Natural	Synthetic	Natural	Synthetic	Natural	Synthetic
Latex rubber	100	100	100	100	100	100
Sulfur	1	1	2	2	3	3
Butyl Zimate	1	1	1	2	1	2

The unmasticated sheets were vulcanized by hot air in a thermostat¹. The dried mixtures obtained from masticated films were vulcanized in a press.

As characteristic of the physical-mechanical properties of the films, the tensile strength, elongation at rupture, and permanent set were measured on a Smirnov dynamometer.

PHYSICAL-MECHANICAL PROPERTIES AND STRUCTURE OF FILMS PREPARED DIRECTLY BY THE ADDITION OF FILLERS TO LATEX

Dried unmasticated films.—The measurements of the physical-mechanical properties of latex films loaded with bentonite clay and channel carbon black show that carbon black is not an active filler in natural latex, but is an active filler in synthetic latex (see Tables 4 and 5).

TABLE 4
PROPERTIES OF VULCANIZED MIXTURES: NATURAL LATEX + FILLER

Parts of filler by weight (per 100 parts of rubber)	Channel carbon black			Bentonite		
	Tensile strength (kg. per sq. cm.)	Relative elongation (%)	Permanent set (%)	Tensile strength (kg. per sq. cm.)	Relative elongation (%)	Permanent set (%)
0	52	1150	48	52	1150	48
5	31	1150	90	38	1150	35
10	32	950	75	34	1100	40
15	28	900	60	36	1070	60
20	39	1000	65	42	1160	50
30	56	1000	60	77	1300	30
40	55	850	60	—	—	—
50	—	—	—	68	950	40
60	50	800	130	56	950	35

TABLE 5
PROPERTIES OF VULCANIZED MIXTURES: SYNTHETIC LATEX + FILLER

Parts of filler by weight (per 100 parts of rubber)	Channel carbon black			Density	Bentonite		
	Tensile strength (kg. per sq. cm.)	Relative elongation (%)	Permanent set (%)		Tensile strength (kg. per sq. cm.)	Relative elongation (%)	Permanent set (%)
0	16	560	20	0.9504	16	560	20
5	52	400	10	—	18	500	25
10	51	380	25	0.9702	20	500	20
15	53	210	15	—	25	480	15
20	22	660	10	—	20	400	18
30	23	520	13	1.0452	17	450	15
40	19	400	3	—	—	—	—

The curves of change of tensile strength of natural latex films as a function of the bentonite clay or carbon black content in the region of low loadings (10–15 parts by weight) show a decrease of tensile strength from the tensile strength of unloaded films, and then an increase of strength to a maximum at 30–50 parts by weight of filler. The increase of tensile strength of films prepared from synthetic latex begins with the smallest addition of filler (Figure 1).

Measurements of the densities of films prepared from loaded mixtures of natural latex showed that the change of density with loading follows a curve which reaches a minimum in the lower range of loading, similar to the tensile strength-loading curve (Figure 2). However, the minimum density is lower than the density of the lightest ingredient of the mixture. The change of density-loading curve of films prepared from synthetic-latex mixtures does not reach a minimum in the range of low loadings.

The relation between the tensile strength and density of loaded latex films appears clearly in the $P = f(\gamma)$ curves, where P is the strength and γ is the density (Figure 3). The data of Figure 3 support the proposed hypothesis

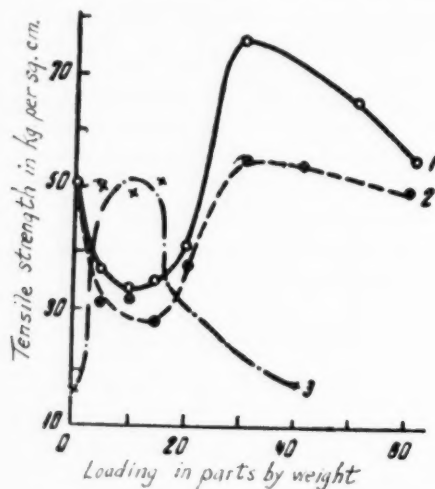


Fig. 1.—Tensile strength of vulcanized latex films as a function of the degree of loading. Curve 1, natural rubber + bentonite. Curve 2, natural rubber + channel carbon black. Curve 3, synthetic rubber + channel carbon black.

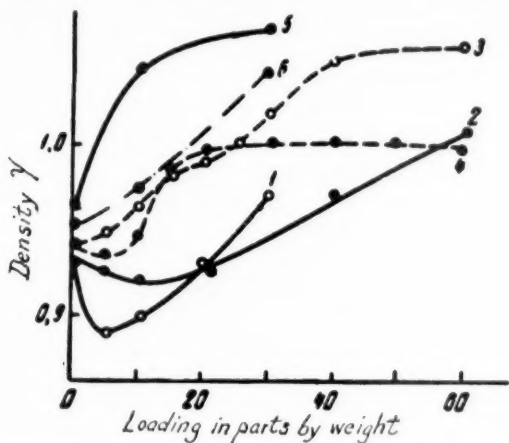


FIG. 2.—Density of latex films as a function of the degree of loading. Curve 1, unvulcanized natural rubber + bentonite. Curve 2, unvulcanized natural rubber + channel carbon black. Curve 3, vulcanized natural rubber + bentonite. Curve 4, vulcanized natural rubber + channel carbon black. Curve 5, unvulcanized synthetic rubber + channel carbon black. Curve 6, vulcanized synthetic rubber + channel carbon black.

that the strength of loaded latex films depends on the distribution of filler in the films, that is, on their structure, and confirm the approximately linear relation between tensile strength and density of loaded latex films.

Mastication of dried and coagulated mixtures.—Mastication of dried and coagulated mixtures prepared from natural-latex mixtures sharply decreases the strength of the latex films. The decrease of strength is a consequence of the destruction of the globular structure on the one hand and of oxidative destruction on the other.

The strength-loading curves of vulcanizates do not reach a minimum in the

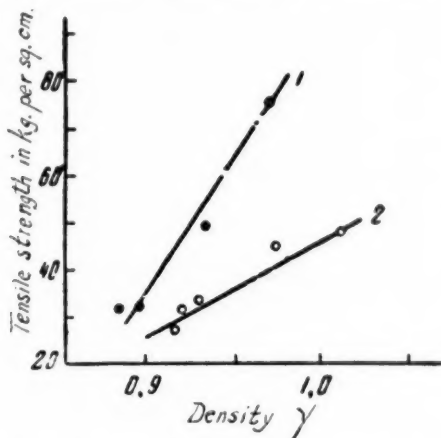


FIG. 3.—Relation between the density and the tensile strength of vulcanized latex films. Curve 1, natural rubber + bentonite. Curve 2, natural rubber + channel carbon black.

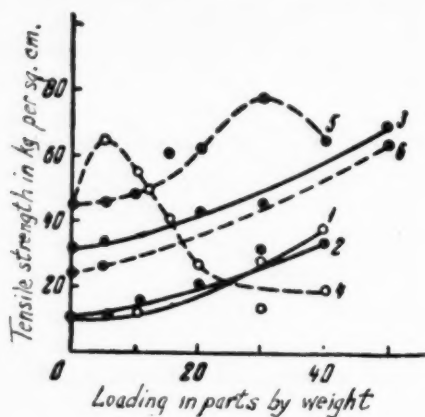


FIG. 4.—Tensile strength of masticated latex sheets as a function of the density. Curves 1, 2, and 3, dried vulcanized mixtures. Curves 4, 5, and 6, coagulated vulcanized mixtures. Curves 1 and 4, natural rubber + bentonite. Curves 2 and 5, natural rubber + channel carbon black. Curves 3 and 6, synthetic rubber + channel carbon black.

region of low-filler contents, and change with the addition of a filler. The activity of bentonite clay and carbon black in dried mixtures prepared from natural latex is roughly the same; for coagulated mixtures, channel carbon black is a more active filler than is bentonite clay. Coagulated mixtures of natural latex possess much greater strength (Figure 4).

From the preceding it follows that mastication destroys the structure of films prepared directly from natural latex and loaded to only a small degree. The strength-load curves of latex mixtures after mastication have the form characteristic of those of ordinary rubber mixtures.

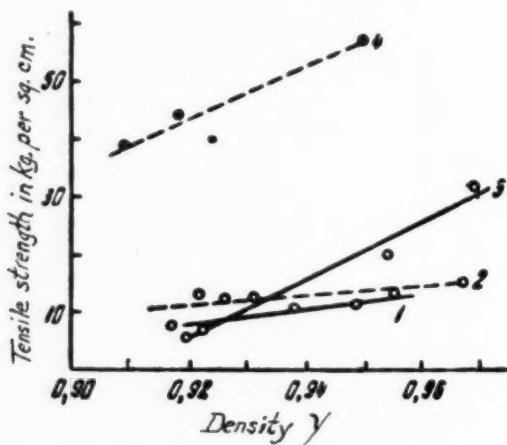


FIG. 5.—Relation between the tensile strength and the density of masticated latex sheets (natural latex rubber channel carbon black). Curve 1, dried unvulcanized films. Curve 2, coagulated unvulcanized films. Curve 3, dried vulcanized films. Curve 4, coagulated vulcanized films.

Possibly the change of composition of the substances adsorbed on the globules of natural rubber after coagulation is reflected in the reinforcing action of fillers; bentonite after coagulation is a considerably less active filler, whereas channel carbon black remains a reinforcing agent. Neither mastication nor coagulation changes the nature of the reinforcement of synthetic-latex mixtures.

Masticated natural-latex mixtures do not show a density minimum in the region of small loading. In all the cases studied, the relation between strength and density was approximately linear (Figure 5).

PHYSICAL-MECHANICAL PROPERTIES AND THE STRUCTURE OF MIXTURES PREPARED BY ADDING FILLERS TO NATURAL RUBBER DURING MASTICATION ON A MILL

Rubber obtained from latex by coagulation is much stronger than rubber obtained by drying.

As in ordinary rubber mixtures, channel carbon black added to dried rubber is an active filler which increases the tensile strength of vulcanizates more than ten times that of unloaded mixtures. The addition of bentonite clay to dried latex rubber causes, not a strengthening of the mixture, but rather a decrease of strength (see Table 6).

TABLE 6
TENSILE STRENGTHS OF VULCANIZATES PREPARED BY DRYING
AND COAGULATING LATEX MIXTURES

Type of filler	Mixtures prepared by drying				Mixtures prepared by coagulation		
	Quantity of filler (weight per 100 parts of rubber)	Strength (kg. per sq. cm.)	Relative elongation (%)	Permanent set (%)	Strength (kg. per sq. cm.)	Relative elongation (%)	Permanent set (%)
Bentonite clay	0	5	500	30	25	1000	10
	5	4	660	—	29	2325	35
	10	3	600	20	31	2280	15
	15	5	880	30	39	1740	17
	20	8	1000	25	36	1700	30
	30	19	1100	10	34	1430	25
	40	16	950	20	40	1345	30
Channel carbon black	0	5	500	30	25	1000	10
	5	6	500	20	42	1700	10
	10	8	400	13	46	1750	13
	15	11	850	17	59	1900	18
	20	19	700	18	79	650	8
	30	40	600	15	87	600	10
	40	43	500	15	83	580	10
	60	51	450	20	80	400	12

Vulcanizates loaded with channel carbon black possess greater tensile strengths than those loaded with bentonite clay. The more active role of channel carbon black in coagulated mixtures is evidently the result of the action of fat acids during the coagulation process.

INTERPRETATION OF RESULTS

This investigation has shown that films of natural-latex mixtures have different structures at different degrees of loading. In the region of small loads

(5 to 15 parts by weight) a loose structure is formed, with decreased strength and density. This phenomenon has already been observed and explained¹. In films from synthetic latexes, the loose structure is not observed in the region of small loads.

The addition of a filler to natural latex in amounts greater than 20 parts by weight apparently results in an equal distribution of filler particles among the latex globules. Mastication destroys the entire loose structure which forms in the films with small loads, and then the mixtures behave like ordinary rubber.

The decrease or increase of the physical-mechanical properties of loaded mixtures depends, in our opinion, on a rubber-filler reaction on the surface layer or at the interface. Bentonite clay and channel carbon black behave differently in mixtures prepared from natural and synthetic latexes. Bentonite clay is an active filler for natural latex, and channel carbon black for synthetic latex. The reinforcing action of fillers must be attributed to the composition of the substances adsorbed on the latex globules and present in the serum, that is, to surface-active substances present in the latex.

The adsorption membrane of the natural-latex globule is composed of proteins and fat acids; that of the synthetic latex of fat acid salts. In natural latex the stability of the latex globule depends on the protein content². Presumably the proteins are present in latex in the form of complex compounds with the fat acids and other components of the serum; this diminishes the independent role of the fat acids in the surface phenomena. This difference in the compositions of the adsorption membranes of natural and synthetic latex globules is the starting point in our attempt to explain the mechanism of reinforcement of latex mixtures.

The reinforcing action of bentonite clay in natural-latex mixtures appears to be due to its reaction with the proteins which make up the protective membrane of the globule. Channel carbon black, for which the best stabilizers are fat acids, does not reinforce rubber in natural-latex mixtures, but does reinforce synthetic-latex mixtures (Igetex S-3), since fat acid salts also enter into the composition of the protective membrane of the globules of this latex. Destruction of the protective membrane of the globule, or a change of its nature, causes a change of the reinforcing effect. Thus, in dried natural-latex mixtures the albuminous membrane is preserved after mastication, and the reinforcing action of bentonite clay is still evident. Coagulation by acetic acid modifies the protective layer, leading apparently to destruction of the albuminous compounds; as a result of this, conditions are created for liberation of the fat acids. After coagulation of latex, bentonite clay does not act as a reinforcing agent, whereas carbon black does still reinforce, since the fat acids play an active part at this stage. This explains why, for natural rubber, *i.e.*, rubber prepared from latex by coagulation with an acid, carbon black is an active filler, whereas bentonite clay is inactive.

In Igetex-3 latex, coagulation by a saturated solution of aluminum chloride does not seriously alter the nature of the adsorption layer; consequently the action of carbon black remains the same after coagulation.

CONCLUSIONS

1. The change of physical properties of loaded films of natural latex with the degree of loading is related to a change of distribution of the filler; when the filler content is small a loose structure is formed, which possesses a lower density and strength.

2. Mastication destroys the loose structure which forms in the range of small loadings, and leads to a disappearance of the minima on the corresponding concentration-strength and concentration-density curves.

In synthetic-latex mixtures, there is no minimum strength or density for a particular degree of loading, since no loose structure is formed. This is still true after mastication.

4. In natural latex, bentonite clay is an active filler; channel carbon black hardly reinforces such latex mixtures. In synthetic latex (Igetex S-3), channel carbon black shows significant reinforcing properties.

5. Mastication of dried latex mixtures does not change the action of fillers.

6. Mastication of coagulated natural-latex mixtures causes channel carbon black to become an active filler; the behavior of fillers in synthetic latex mixtures is not changed by mastication.

7. The above mentioned phenomena are the result of the action of surface-active substances present in latex and adsorbed on the surface of its globules.

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EFFECT OF OXYGEN CONCENTRATION ON AGING OF RUBBER VULCANIZATES *

I. EFFECT OF PARTIAL PRESSURE OF OXYGEN ON RATE OF OXYGEN ABSORPTION

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The influence of oxygen pressure in the aging atmosphere on the aging of rubber compounds has been reported from time to time. It has been demonstrated by numerous workers¹ that an increase in the oxygen pressure generally increases the rate of deterioration of most stocks. It has also been reported, however, that the rate of oxygen absorption is nearly independent of oxygen pressure. Williams and Neal², for example, reported that the rate of oxidation of samples ground on a mill and extracted with acetone showed no dependence on oxygen pressure above a certain minimum value. Kinetic studies by Bolland and Gee³, Tobolsky⁴, and others have shown that the principal initiation reaction in the autocatalytic oxidation of olefins and of rubber involves the decomposition of peroxides, and that the rate is thus independent of oxygen pressure except at very low oxygen concentrations and in the very early stages of oxidation. However, work reported by Milligan and Shaw⁵, Carpenter⁶, and van Amerongen⁷, and in previous publications from this laboratory⁸ has demonstrated a dependence of rate of oxidation on oxygen pressure, although the quantitative nature of the dependence was not clearly defined.

The present investigation was undertaken to determine the effect of varying the partial pressure of oxygen in the aging atmosphere upon the rate of oxygen absorption of certain natural and synthetic rubber stocks. The study has been confined to the constant-rate stage which precedes the start of the autocatalytic reaction, since this is the stage of greatest practical significance. Both the rate of oxidation in this stage and the duration appear to be controlled by the antioxidant. Only the amine type of antioxidants have been included in this study. The effect of different oxygen pressures on changes of physical properties accompanying the oxygen absorption is discussed in the second part of this paper.

PROCEDURE

The volumetric oxygen-absorption technique described in previous publications from this laboratory⁹ was used. Three tread stocks were employed, including both inhibited and uninhibited Hevea black stocks and a GR-S black stock. The formulations and cures are given in Table I. The so-called uninhibited stock is actually weakly inhibited, owing to the presence of natural antioxidants in the original rubber, and to the use of Santocure as an accelerator. This accelerator contains an amine, and has been shown to have some antioxidant character¹⁰.

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TABLE I
COMPOUNDING OF STOCKS

	Hevea black		GR-S black inhibited
	Inhibited	Uninhibited	
Smoked sheet	100	100	—
GR-S AC ^a	—	—	100
Paraflux ^b	4	4	4
Stearic acid	3	3	2.4
Bardol ^c	—	—	4
Zinc oxide	3	3	2.4
Santocure ^d	1	1	1.2
Sulfur	3	3	2
Santoflex B ^e	1.5	—	—
EPC black	50	50	45
Cure time at 280° F (min.)	40	40	60

^a Contains 1.25% phenyl-2-naphthylamine.

^b C. P. Hall Co.

^c Barrett Division, Allied Chemical and Dye Corp.

^d Reaction product of cyclohexylamine and mercaptobenzothiazole.

^e Reaction product of acetone and *p*-aminobiphenyl, mainly 2,2,4-trimethyl-6-phenyl-1,2-dihydroquinoline.

The effect of varying the partial pressure of oxygen, in combination with nitrogen, was determined by measuring the oxygen absorbed and periodically adding oxygen to maintain the desired average concentration in the aging atmosphere. The oxygen concentrations were approximately 10, 20, and 100 per cent, with a maximum variation of 1 to 2 per cent. The total pressure was 1 atmosphere (760 mm. of mercury) in each case.

Three sample thicknesses were used (approximately 0.010, 0.020, and 0.040 inch) as a check on possible limitation of the rate of oxidation by the rate of diffusion of oxygen into the sample. Each stock was studied at three different temperatures.

EXPERIMENTAL RESULTS

The oxygen-absorption curves obtained with three thicknesses of the inhibited Hevea black stock at 100° C and three different partial pressures of oxygen (1.0 ± 0.02 , 0.21 ± 0.02 , and 0.056 ± 0.01 atm.) are shown in Figure 1.

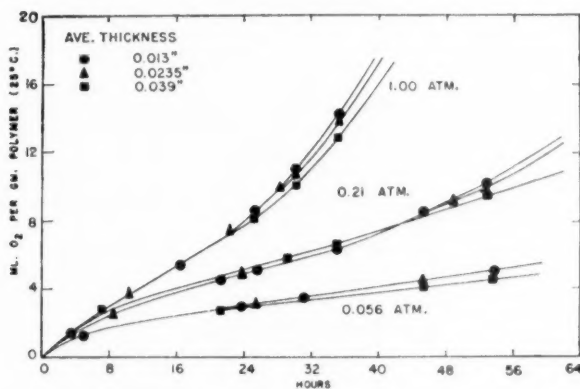


FIG. 1.—Oxygen absorption of inhibited Hevea black stock. At 100° C and various partial pressures of oxygen. Total pressure 760 mm.

An increase of the oxygen concentration in the aging atmosphere results in an increased rate of oxygen absorption—for example, the rate of oxygen absorption in the constant-rate stage, K_2 , in oxygen, is slightly more than twice that observed with the oxygen-nitrogen ratio corresponding to air. Approximately the same effect was observed in comparing air-oven aging with aging in the oxygen-absorption apparatus. The ratio of hours in air to hours in oxygen to give the same degradation of tensile strength was approximately 2.0 for a stock of the same compounding¹¹.

A quantitative relationship between the observed rates in the constant-rate stage and the oxygen pressure is given by:

$$K_2 = kP^{0.5}$$

It is evident that this pressure dependence cannot be due to diffusion limitation, as, with one exception, samples of three different thicknesses absorbed

TABLE II
RATES OF OXYGEN ABSORPTION IN CONSTANT-RATE STAGE AT VARIOUS
PARTIAL PRESSURES OF OXYGEN

Inhibited Hevea black stock at 90° and 100° C GR-S
black stock at 100° C

Stock	Temp. (° C)	O ₂ pressure (atm.)	Obsvd. rate (K ₂)	Evaluation of $k = K_2/P^{0.5}$	Calcd. rate, $K_2 = kP^{0.5}$
Hevea black inhibited	90	1.00 ±0.02	0.131	0.131	0.132
		0.21 ±0.02	0.058	0.127	0.060
		0.10 ±0.01	0.044	0.139	0.042
	100			Av. 0.132	
		1.00 ±0.02	0.292	0.292	0.292
		0.21 ±0.02	0.128	0.283	0.134
GR-S black	100	0.056 ±0.01	0.067	0.301	0.069
				Av. 0.292	
	100	1.00 ±0.02	0.095	0.095	0.092
		0.21 ±0.02	0.042	0.092	0.042
		0.10 ±0.01	0.028	0.089	0.029
				Av. 0.092	

oxygen at the same rate in the constant-rate stage. In the case of the lowest oxygen concentration, data for the thickest sample deviate somewhat, but the two thinnest samples exhibited the same rate of oxygen absorption. At the end of the constant-rate period, however, the rates increase and the curves diverge, indicating that the rate of the reaction in this autocatalytic stage is partially limited by the rate of diffusion of oxygen into the samples.

The experimentally determined rates are compared in Table II with the values obtained from the equation, $K_2 = kP^{0.5}$. Comparable data obtained with the same stock at 90° C and with a GR-S black stock at 100° C are also included. (The oxygen-absorption curves for the GR-S stock are shown in Figure 2). There is good agreement between experimental and calculated values of K_2 in all three cases.

The uninhibited Hevea black stock at 70° and 80° C also showed a marked dependence of rate of oxidation on oxygen pressure. (The oxygen-absorption

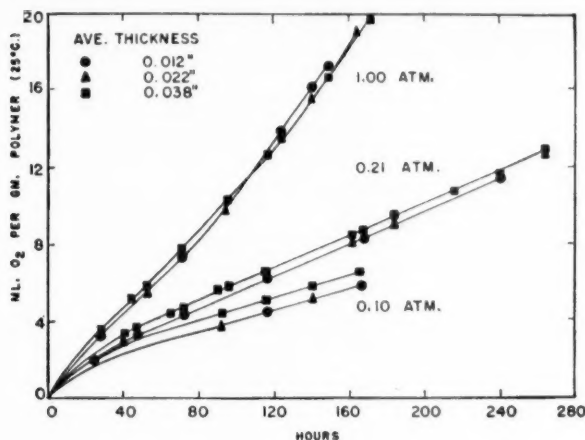


Fig. 2.—Oxygen absorption of GR-S black stock. At 100° C and various partial pressures of oxygen. Total pressure 760 mm.

curves obtained at 70° C are shown in Figure 3.) The simple equation, $K_2 = kP^{0.5}$, did not give good agreement with the observed behavior, but an equation of the form:

$$K_2 = k(P + a)^{0.5}$$

did give a satisfactory correlation, as shown in Table III.

A similar relationship was observed at 120° C with the inhibited Hevea stock and at 110° and 132° C with the GR-S stock. Representative oxygen-absorption data are shown in Figure 4 for the Hevea stock at 120° C and in Figure 5 for the GR-S stock at 132° C. Only the thinner samples were employed at these higher temperatures. The simple equation which gave satis-

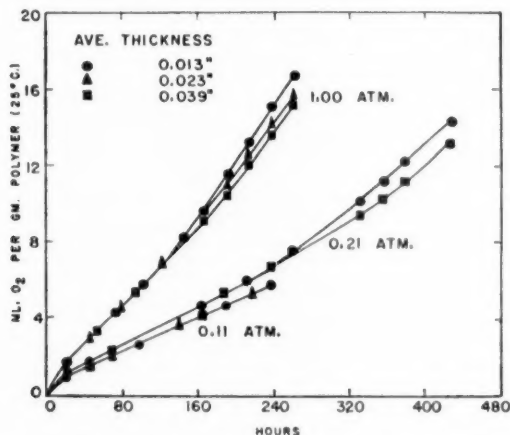


Fig. 3.—Oxygen absorption of uninhibited Hevea black stock. At 70° C and various partial pressures of oxygen. Total pressure 760 mm.

TABLE III
RATES OF OXYGEN ABSORPTION IN CONSTANT-RATE STAGE AT VARIOUS
PARTIAL PRESSURES OF OXYGEN

Uninhibited Hevea black stock at 70° and 80° C Inhibited
Hevea black stock at 120° C GR-S
black stock at 110° and 132° C

Stock	Temp. (° C)	O ₂ pressure (atm.)	Obsvd. rate (K ₂)	Caled. rate, $K_2 = k(P+a)^{0.5}$		
				<i>k</i>	<i>a</i>	<i>K</i> ₁
Hevea black uninhibited	70	1.00 ±0.02	0.051	0.0485	0.10	0.051
		0.21 ±0.02	0.026			0.027
		0.11 ±0.01	0.023			0.022
	80	1.00 ±0.02	0.122	0.114	0.14	0.122
		0.21 ±0.02	0.068			0.067
		0.11 ±0.01	0.057			0.057
Hevea black inhibited	120	1.00 ±0.02	2.48	2.43	0.042	2.48
		0.21 ±0.02	1.25			1.22
		0.11 ±0.01	0.92			0.95
GR-S black	110	1.00 ±0.02	0.264	0.260	0.033	0.264
		0.21 ±0.02	0.128			0.128
		0.092±0.01	0.093			0.092
	132	1.00 ±0.02	1.74	1.55	0.257	1.74
		0.21 ±0.01	1.09			1.06
		0.096±0.01	0.90			0.92

factory correlation of the data for these stocks at temperatures of 100° C and below was not satisfactory for these data, but the equation $K_2 = k(P + a)^{0.5}$ was required. The experimental and calculated rates are compared on this basis in Table III.

It would seem from these data that the latter equation is the more general one, and that the simpler expression is a special form obtained when *a* ap-

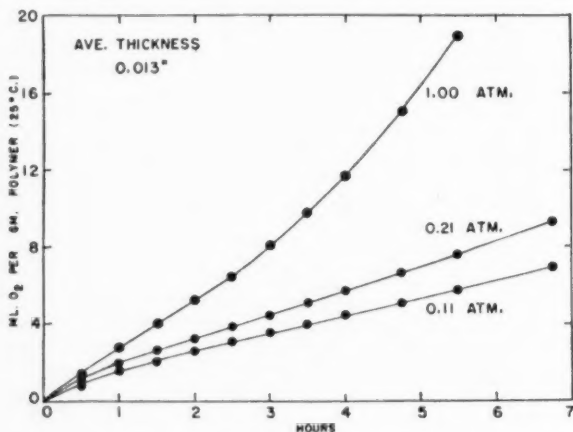


Fig. 4.—Oxygen absorption of inhibited Hevea black stock. At 120° C and various partial pressures of oxygen. Total pressure 760 mm.

proaches zero. This condition apparently prevails only at lower rates of oxidation, as observed with the strongly inhibited stocks at somewhat lower temperatures.

THEORETICAL SIGNIFICANCE

It has been shown experimentally that, for strongly inhibited stocks (containing amine inhibitors such as PBNA and Santoflex B) at temperatures of 100° C or less, the rate in the constant-rate stage is proportional to the square root of the oxygen concentration: $K_2 = kP^{0.5}$. However, at higher temperatures with these stocks, or with weakly inhibited stocks (containing Santocure) even at temperatures as low as 70° C, an equation of the following type was required to correlate the data: $K_2 = k(P + a)^{0.5}$.

The dependence of rate of oxidation in the constant-rate stage for amine-inhibited stocks on oxygen concentration has some interesting theoretical implications. In order to interpret the probable significance of these data, it is first necessary to review some of the present theories of the mechanism of

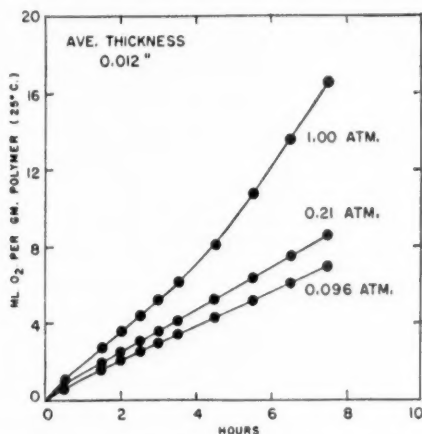


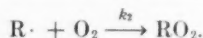
FIG. 5.—Oxygen absorption of GR-S black stock. At 132° C and various partial pressures of oxygen. Total pressure 760 mm.

oxidation and then to derive an equation for the rate of oxygen absorption in the constant-rate stage based on theoretical considerations.

Present theories of oxidation and antioxidant action.—The work of Farmer, Bolland, Gee, Tobolsky, and many others on the mechanism of oxidation of hydrocarbons supports the concept that the reaction is an autocatalytic chain reaction propagated by free radicals. Such a reaction has three phases: initiation, propagation, and termination.

The initiation step may involve more than one process, but in the autocatalytic stage of rapid oxidation it is thought to be primarily the result of peroxide decomposition to form radicals. Such an initiation process would not require oxygen, and the maximum rate attained in the autocatalytic reaction is said to be independent of oxygen concentration. However, this is apparently not the case for the slower reaction which precedes the autocatalytic stage, as shown by the dependence of rate on oxygen concentration in the case of the amine-inhibited stocks employed in the present study.

The nature of the propagation steps for a free-radical chain mechanism is generally agreed to involve the following reactions:

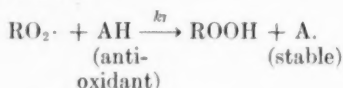


($R'\cdot$ could also be formed by addition of $R\cdot$ to the double bond, with formation of a new radical, but such a step would not change the concentration of free radicals, and would be indistinguishable in the experimentally observed rate of oxidation.)

The possible termination steps include combinations of all types of radicals present to form stable products, but at appreciable oxygen pressures $R\cdot$ radicals will be rapidly converted to $RO_2\cdot$, and the main termination reaction would then be:



If an antioxidant functions by termination of the reaction chain through the formation of a stable radical which does not initiate a new chain reaction, the chief termination reaction in the constant-rate stage (which is controlled by the antioxidant) would be:



If we let R_i = rate of initiation of free radicals, we find that the rate of oxygen absorption based on the above termination mechanisms is given by the following equations:

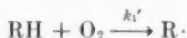
In the absence of antioxidants,

$$\frac{-d[O_2]}{dt} = \frac{k_3}{k_4^{1/2}} [RH] (R_i)^{1/2} \quad (1)$$

In the presence of antioxidants,

$$\frac{-d[O_2]}{dt} = \frac{k_3 [RH]}{k_7 [AH]} (R_i) \quad (2)$$

The present study on amine-inhibited stocks indicates that, in the constant-rate stage, at moderate temperatures, the rate depends on the square root of the oxygen concentration. This then would indicate that the predominant means of forming free radicals in this stage involves oxygen. Such a step was proposed by Bolland and Gee³ for the initial stage in the oxidation of ethyl linoleate. (This process was considered to be negligible in the subsequent rapid oxidation, however, and was omitted in their final kinetic mechanism.)



On the basis of this method of initiation,

$$R_i = k_1' [RH] [O_2]$$

Substituting this value for R_i in Equation 1,

$$\frac{-d[O_2]}{dt} = k_3 \left(\frac{k_1'}{k_4} \right)^{1/2} [RH]^{3/2} [O_2]^{1/2}$$

Assuming that RH does not change very much over the range involved, then:

$$K_2 = kP^{0.5}$$

This indicates that the observed dependence of rate on the square root of the oxygen concentration is consistent with termination by a combination of two radicals to form stable products.

However, a comparable substitution in Equation 2 gives:

$$\frac{-d[O_2]}{dt} = \frac{k_3 k_1' [RH]^2}{k_7 [AH]} [O_2]$$

or

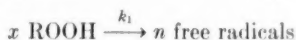
$$K_2 = kP$$

This expression is in direct disagreement with experimental evidence for amine-inhibited stocks, which exhibit a dependence on the square root of the oxygen concentration (rather than the first power). This suggests that the amine type of antioxidants do not function by a chain-stopping mechanism. This is contrary to the theory which has been generally subscribed to on the basis of studies with phenolic antioxidants. Bolland and Bateman¹², however, recognized that the amine type of antioxidants may not function by the same mechanism as the phenolic antioxidants, but rather may interfere at some other point in the oxidation process.

The simple square root dependence of rate on oxygen concentration did not hold at higher temperatures, or for weakly inhibited stocks at moderate temperatures. However, the expression:

$$K_2 = k(P + a)^{1/2}$$

did give good agreement with the observed rate in these cases. Such an expression can be arrived at from a theoretical point of view, as is shown in the derivation that follows. The pressure term apparently comes from initiation by direct oxygen attack on the hydrocarbon, while a represents initiation by a process which does not require oxygen. Peroxide decomposition to form free radicals would be such a process.



Taking into account both types of initiation, Equation 1 becomes:

$$\frac{-d[O_2]}{dt} = \frac{k_3}{k_6^{1/2}} [RH] \{ k_1' [RH] [O_2] + n k_1 [\text{ROOH}]^x \}^{1/2}$$

This equation is similar in form to the experimentally observed relationship, $K_2 = k(P + a)^{0.5}$, where a thus represents the relative contribution of peroxide decomposition, and P the contribution of direct oxygen attack, to the formation of chain-initiating free radicals. It was noted previously that a has an appreciable value in the oxidation of a weakly inhibited stock at temperatures at least as low as 70° C, but that it is negligible in the constant-rate stage of the oxidation of a comparable strongly inhibited stock at temperatures up to 100° C.

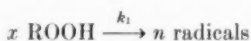
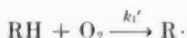
These facts thus indicate that initiation by direct oxygen attack is an important reaction in the constant-rate stage of oxidation, and that the action of the amine type of inhibitors is to prevent or decrease, in some manner, the

formation of free radicals by peroxide decomposition. Such action may involve one or both of the following possibilities:

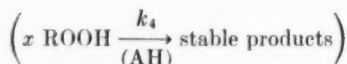
1. Retarding the formation of hydroperoxides
2. Promoting hydroperoxide decomposition to stable products

Revised mechanism.—An over-all mechanism for the oxidation of amine-inhibited stocks should include the following steps:

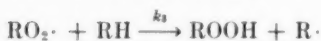
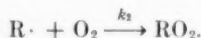
INITIATION.



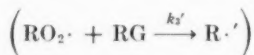
OR



PROPAGATION.



OR



TERMINATION.



These reactions differ from those employed by Bolland and his coworkers only in that initiation by direct oxygen attack is included, and that the anti-oxidant is considered to function in the initiation stage, rather than to act as a chain stopper in the termination process. The rate of oxygen absorption is given by:

$$\begin{aligned} \frac{-d[O_2]}{dt} &= K_0 \left(\frac{dV}{dt} \right) \\ &= \frac{k_3 + k_3'}{k_6^{1/2}} [RH] \{ k_1' [RH] [O_2] + nk_1 [ROOH]^x \}^{1/2} \quad (3) \end{aligned}$$

where K_0 is a constant expressing the proportionality of moles of oxygen absorbed per second ($-dO_2/dt$) to milliliters of oxygen ($25^\circ C$) absorbed per gram of hydrocarbon per hour (dV/dt). Similarly, the variation of the hydroperoxide concentration with time is given by:

$$\begin{aligned} \frac{d[ROOH]}{dt} &= \frac{k_3}{k_9^{1/2}} [RH] \{ k_1' [RH] [O_2] \\ &\quad + nk_1 [ROOH]^x \}^{1/2} - (k_a + k_1) [ROOH]^x \quad (4) \\ &= \frac{k_3}{k_3 + k_3'} \left(\frac{-dO_2}{dt} \right) - (k_a + k_1) [ROOH]^x \quad (5) \end{aligned}$$

In the constant-rate stage, $dV/dt = K_2$, and $d[ROOH]/dt$ must be 0, or the rate would not be constant.

Substituting K_0K_2 for $-d[O_2]/dt$ in Equation 5 and setting $d[ROOH]/dt = 0$, we have:

$$0 = \frac{K_0k_3}{k_3 + k_3'} K_2 - (k_a + k_1)[ROOH]^x \quad (6)$$

or

$$[ROOH]^x = \frac{K_0k_3}{(k_3 + k_3')(k_a + k_1)} K_2 \quad (7)$$

Substituting Equation 7 in Equation 3 we have:

$$\frac{dV}{dt} = K_2 = \frac{k_3 + k_3'}{K_0k_6^{1/2}} [RH] \left\{ k_1' [RH][O_2] + \frac{nK_0k_3k_1}{(k_3 + k_3')(k_a + k_1)} K_2 \right\}^{1/2} \quad (8)$$

Because the oxygen concentration in the rubber, $[O_2]$, is proportional to the external oxygen pressure, P , we may substitute KP for $[O_2]$, and rearrange so that:

$$K_2 = \frac{k_3 + k_3'}{K_0} \left(\frac{Kk_1'}{k_6} \right)^{1/2} [RH]^{3/2} \left\{ P + \frac{nK_0k_3k_1}{(k_3 + k_3')(k_a + k_1)Kk_1' [RH]} K_2 \right\}^{1/2}$$

or

$$K_2 = b(P + cK_2)^{1/2} \quad (9)$$

Squaring both sides of the equation and solving the resulting quadratic equation for K_2 , we find:

$$K_2 = \frac{b^2c}{2} \left(1 + \sqrt{1 + \frac{4}{b^2c^2} P} \right)$$

or

$$K_2 = \alpha(1 + \sqrt{1 + \beta P}) \quad (10)$$

It is possible to evaluate alpha and beta from a knowledge of K_2 at various pressures.

Once alpha and beta are known, b and c may be computed from the relationships:

$$b = \alpha\beta^{1/2} \quad c = \frac{2}{\alpha\beta}$$

From Equation 10 it is seen that when alpha is small, so that $K_2 - \alpha \approx K_2$,

$$K_2 = \alpha\beta^{1/2} \left(P + \frac{1}{\beta} \right)^{1/2} = k(P + a)^{1/2} \quad (11)$$

When alpha is very small and beta very large: $K_2 - \alpha \approx K_2$ and $\frac{1}{\beta} \approx 0$,

$$K_2 = \alpha\beta^{1/2}P^{1/2} = kP^{1/2} \quad (12)$$

It is, however, necessary to note that Equations 9 and 10,

$$K_2 = b(P + cK_2)^{1/2} = \alpha(1 + \sqrt{1 + \beta P})$$

give better agreement in the majority of the cases studied than does $K_2 = k(P + a)^{1/2}$, particularly at the higher temperatures, as shown in Table IV as compared to Table III. This arises from the fact that a (which represents the

TABLE IV
RATES OF OXYGEN ABSORPTION IN CONSTANT-STATE STAGE AT VARIOUS
PARTIAL PRESSURES OF OXYGEN

Comparison of calculated values from a theoretically derived equation
with observed behavior

Stock	Temp. (° C)	O ₂ pressure (atm.)	Obsvd. rate (K ₂)	Calcd. rate, $K_2 = b(P + cK_2)^{0.5}$ or $K_2 = \alpha(1 + \sqrt{1 + \beta P})$				
				α	β	b	c	K_2
Hevea black uninhibited	70	1.00	0.051	0.0056	65	0.045	5.50	0.051
		0.21	0.026					0.027
		0.11	0.023					0.022
	80	1.00	0.122	0.01835	30.7	0.102	3.55	0.122
		0.21	0.068					0.068
		0.11	0.057					0.057
Hevea black inhibited	120	1.00	2.48	0.185	153	2.29	0.0707	2.48
		0.21	1.25					1.25
		0.11	0.92					0.92
GR-S black	110	1.00	0.264	0.0134	250	0.2505	0.426	0.264
		0.21	0.128					0.129
		0.092	0.093					0.091
	132	1.00	1.74	0.362	13.74	1.34	0.402	1.75
		0.21	1.09					1.08
		0.096	0.90					0.91

contribution of peroxide decomposition to the initiation process) was treated as constant in the simplified equation, whereas it is actually a function of the rate, which changes with oxygen pressure. The theoretically derived equations thus appear to be completely consistent with the observed experimental behavior.

Temperature would also be expected to have an effect on the magnitude of the contribution of each of the two initiation processes to the reaction, and consequently an Arrhenius plot of $\log K_2$ vs. $1/T$ would not be expected to be linear. Nevertheless, it has been observed experimentally¹³ that such a plot approximates a straight line over a reasonable temperature range (50° to 110° C), and while extrapolation of such data will not be completely valid, it does give an approximation of the rate to be expected.

CONCLUSIONS

The rate of oxygen absorption, K_2 , in the constant-rate stage is a function of the square root of the partial pressure of oxygen in the aging atmosphere, in the case of amine-inhibited stocks of natural rubber and GR-S. A general equation of the form, $K_2 = k(P + a)^{0.5}$, gives good agreement with the data. For strongly inhibited stocks (containing PBNA or Santoflex B) at temperatures of 100° C or less, a is negligible, but at higher temperatures with these stocks, or with weakly inhibited stocks—e.g., those cured with Santocure—even at moderate temperatures, the more general form of the equation is required.

The observed dependence of rate of oxygen absorption in the constant-rate stage on the partial pressure of oxygen in the aging atmosphere shows that initiation by direct oxygen attack on the hydrocarbon is an important phase of the oxidation mechanism in the constant-rate stage, for amine-inhibited stocks.

Taking into account initiation by this method, as well as by peroxide decomposition, it is possible to derive a theoretical equation of the type:

$$K_2 = b(P + cK_2)^{0.5}$$

which compares in form with the observed behavior noted above.

The fact that a square-root dependence on oxygen concentration was observed (rather than the first power) suggests that the amine type of antioxidants probably do not function by a chain-stopping mechanism, but rather exert their effect at some other point in the oxidation process. This function may involve promotion of peroxide decomposition to stable products rather than to chain-initiating free radicals.

Since the completion of this work, Kuzminskii, Shanin, and Lezhnev¹⁴ have reported the dependence of the rate of oxidation of sodium butadiene polymer inhibited by phenyl-2-naphthylamine, on the square root of the oxygen concentration in the sample. This is in direct accord with the work reported here on the amine-inhibited black vulcanizates of Hevea and GR-S.

II. EFFECT OF PARTIAL PRESSURE OF OXYGEN ON CHANGES IN PHYSICAL PROPERTIES ACCOMPANYING OXIDATION

Many workers have studied the influence of the aging atmosphere upon the nature of the aging of rubber vulcanizates¹⁶. It has been generally observed that an increase of the oxygen pressure increases the rate of deterioration of most stocks. The fact that a change of oxygen concentration causes a change of the relative amounts of cross-linking and chain scission occurring in the stock during oxidation has been established by prior work in this laboratory¹⁷ and also by Scott¹⁸.

The following discussion is concerned with the effect of changes of partial pressure of oxygen on changes of properties for a given amount of oxygen absorbed. Heat aging in oxygen-free nitrogen is included, along with aging in pure oxygen, and a combination of oxygen and nitrogen corresponding to the normal ratio in air.

PROCEDURE

The volumetric oxygen-absorption apparatus used in this study, and the procedure employed, have been described¹⁸. The same GR-S and Hevea black stocks were used, as described previously (Table I).

An uninhibited Hevea gum stock, also included in the present study, was compounded as follows: smoked sheet 100, stearic acid 2, zinc oxide 5, sulfur 3, Thiotax (mercaptopbenzothiazole) 0.75; cure, 40 minutes at 280° F.

Several tubes of the oxygen-absorption apparatus were filled with triplicate dumbbell test-specimens of a given stock cut from sheets approximately 0.040 inch thick. The samples were aged in the appropriate atmosphere at suitable temperatures and, removed for testing after various time intervals.

The aging-atmospheres were:

1. Oxygen-free nitrogen
2. Simulated air (21% O₂, 79% N₂)
3. Pure oxygen

The lamp-grade nitrogen (obtained from Cleveland Wire Works, General Electric Co.) contained less than 5 p.p.m. of oxygen, and was used as obtained.

Samples aged in air and oxygen were removed for test at various stages of oxidation up to 20 cc. of oxygen (25° C, 760 mm.) per gram of polymer in the sample. Oxygen absorbed from the oxygen-nitrogen combination corresponding to air was replaced periodically to maintain the average concentration at the desired value with a maximum variation of 1 to 2 per cent in oxygen content. The total pressure was maintained near 760 mm. by manual adjustment with accurate setting at the time volume readings were taken.

Initial and aged values of tensile strength, modulus, or stress at 200 and 300 per cent elongation, elongation at break, and Shore A hardness were measured. These values are compared on a time basis for aging in nitrogen, and as a function of oxygen absorbed in the case of samples aged in simulated air and in oxygen.

HEAT AGING IN NITROGEN

A comparison of changes of properties after various amounts of oxygen have been absorbed fails to take into account any effect due to differences in time of heating required to reach a given oxygen absorption. In general, it takes almost twice as long in air as in oxygen for a stock to absorb a given amount of oxygen. There are undoubtedly some purely thermal effects which are superimposed upon the oxidative aging. Therefore, the effect of heating in the absence of oxygen has been investigated by heating the stocks in lamp nitrogen (not over 5 p.p.m. of oxygen) in order to determine the magnitude and duration of the heat aging.

TABLE V
PHYSICAL PROPERTIES OF GR-S AND HEVEA STOCKS

Aging	Modulus (lb./sq. inch)		Tensile strength (lb./sq. inch)	Ultimate elongation (%)	Shore A hardness
	200%	300%			
Inhibited Hevea black stock after heating in nitrogen at 90° C					
Original	1160	1930	4350	550	66
1-hour evac.	1270	2110	4170	510	68
1 day, N ₂	1310	2250	4200	490	67-8
6 days, N ₂	1130	2000	4060	505	65
Uninhibited Hevea black stock after heating in nitrogen at 70° C					
Original	1260	2170	4230	500	65
1-hour evac.	1430	2350	4130	480	68
4 days, N ₂	1380	2360	4070	490	69.5
9 days, N ₂	1480	2460	4270	480	69.5
Uninhibited Hevea gum stock after heating in nitrogen at 90° C					
Original	175	290	3870	730	39
1-hour evac.	170	260	3630	740	40
1 day, N ₂	180	375	3450	650	40
2 days, N ₂	190	365	3430	650	40.5
4 days, N ₂	200	340	3270	665	38
GR-S black stock after heating in nitrogen at 100° C					
Original	560	1060	3450	640	59-60
1-hour evac.	670	1280	3450	585	59
2 days, N ₂	1150	2200	2530	350	65
3 days, N ₂	1210	2160	2380	325	65
5 days, N ₂	1220	2160	2490	340	65
10 days, N ₂	1220	2170	2340	320	65

The physical properties before and after heating in virtually oxygen-free nitrogen are given in Table V for the GR-S and Hevea stocks. There was no measureable absorption of nitrogen other than the small amount (0.1 to 0.4 cc. per gram) which was taken up immediately, presumably to saturate the sample after evacuation at the beginning of the test.

The Hevea black stocks show a moderate stiffening after being heated for 1 hour at the test temperature under vacuum (less than 2 mm. of mercury). Further heating in nitrogen appears to have only a very slight effect. In the case of the uninhibited black stock, data on samples of 0.075-inch thickness (not shown in the tables) indicate that the stock has essentially the same physical properties after 23 days in nitrogen as after 2 days.

The uninhibited Hevea gum stock changed somewhat more at 90° C than the black stock, on the basis of tensile strength, but even so, the properties after 4 days in nitrogen at 90° C were in general still within 10 per cent of the original values.

The GR-S black stock shows considerably greater susceptibility to heat aging. Most of the change took place during the first 2 days of heating in nitrogen. Thereafter, the properties remained almost constant, but during the initial period the elongation was reduced by 45 per cent, the tensile strength was reduced 25 per cent, and the modulus values were doubled. (Data on 0.075-inch samples indicate that most of the change occurs in the first 24 hours of heating in nitrogen at this temperature.)

Samples of this stock heated in nitrogen for 2 days show more stiffening than those heated in oxygen at the same temperature for the same length of time. This result is in accord with the observed tendency of this stock to stiffen, particularly when aged at low oxygen pressures. These data suggest that R· radicals are more effective than RO₂· radicals in reacting with double bonds to form cross links, and that such an addition of a free radical to a double bond is probably one mechanism of cross-linking. Similar conclusions were reached by Tobolsky and Mesrobian¹⁹ based on the greater hardening of GR-S in the air oven as compared with the oxygen bomb.

The fact that this change occurs during the first day or two of heat aging and then ceases indicates that it is caused by some factor which is soon removed. One possibility is dissolved or adsorbed oxygen which is not completely removed by evacuation. Another plausible explanation would be the presence of pre-formed peroxides in the original sample which are decomposed by heat to initiate a free-radical type of polymerization. Aftervulcanization is probably involved also.

In any event, this effect, which is brought about by heat, will occur throughout the stock regardless of its thickness. Comparison of changes in properties for various amounts of oxygen absorbed, as reported in the following section, thus includes in the first aging periods some effect of heat aging which is superimposed on that which is proportional to the measured oxygen absorption. It should not be assumed, however, that all of the change observed in nitrogen also occurs in the presence of oxygen, as the conversion of R· to RO₂· would considerably alter the situation.

AGING IN AIR AND OXYGEN

The effect of oxygen concentration on the rate of oxygen absorption of rubber vulcanizates has been demonstrated by the data in the first part of this paper. A corresponding effect on the change in physical properties also is

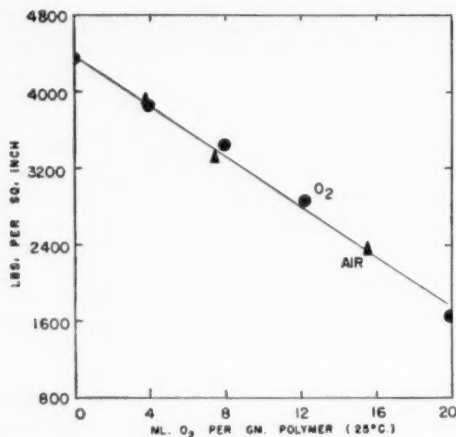


Fig. 6.—Tensile strength of inhibited Hevea black stock vs. oxygen absorption in air and oxygen. At 90° C, 760 mm.

observed, since the rate of deterioration is, in general, proportional to the oxygen absorbed. However, the change in oxygen concentration also influences the relative extent of the chain-scission and cross-linking reactions. Consequently the resultant effect (as measured by changes in properties for a given absorption of oxygen) may also vary with the oxygen concentration.

Inhibited Hevea black stock.—The change of tensile strength as a function of oxygen absorbed from air and from oxygen is plotted in Figure 6 for the inhibited

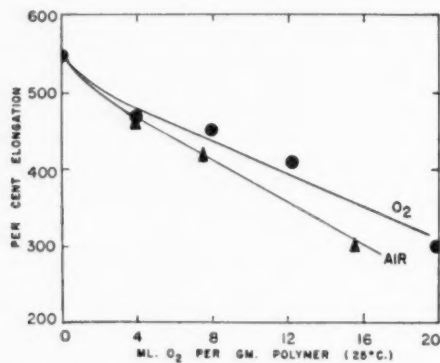


Fig. 7.—Ultimate elongation of inhibited Hevea black stock vs. oxygen absorption in air and oxygen. At 90° C, 760 mm.

Hevea black stock. There is no detectable difference, in this case, in the degradation brought about by a given absorption of oxygen from air or oxygen.

Other properties, as shown in Figures 7, 8, and 9, demonstrate a difference when a given amount of oxygen is absorbed at different rates from air and oxygen. Apparently such properties as elongation, modulus, and hardness are more sensitive to changes of the relative amounts of chain scission and cross-

linking than is tensile strength. From these data it is apparent that a given absorption of oxygen from air results in a lower ultimate elongation and higher modulus and hardness values than are obtained at a comparable absorption from pure oxygen. Similar results (not presented here) were obtained with the uninhibited Hevea black stock.

Uninhibited Hevea gum stock.—The aging behavior of an uninhibited Hevea gum stock in oxygen and in simulated air at 90° C is demonstrated in Figures

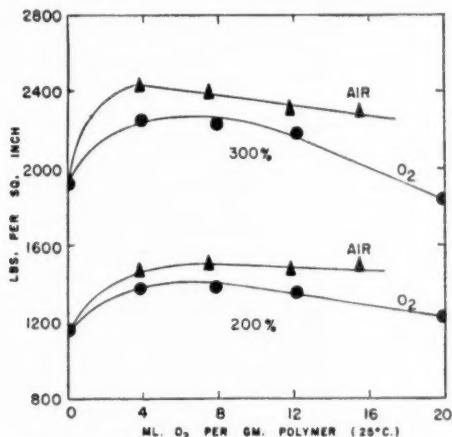


FIG. 8.—Moduli of inhibited Hevea black stock vs. oxygen absorption in air and oxygen. At 90° C, 760 mm.

10 to 13, inclusive. The drastic reduction of tensile strength during the absorption of the first 5 cc. of oxygen is thought to result from a decreased ability to crystallize on stretching. The fact that the decrease was greater in air than in oxygen, together with other indications of a higher proportion of cross-linking in air compared to oxygen, suggests the introduction of irregularities in structure which impede orientation of the molecular chains.

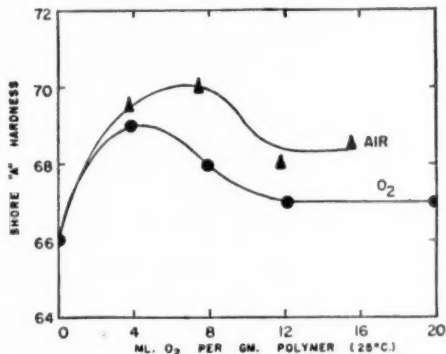


FIG. 9.—Hardness of inhibited Hevea black stock vs. oxygen absorption in air and oxygen. At 90° C, 760 mm.

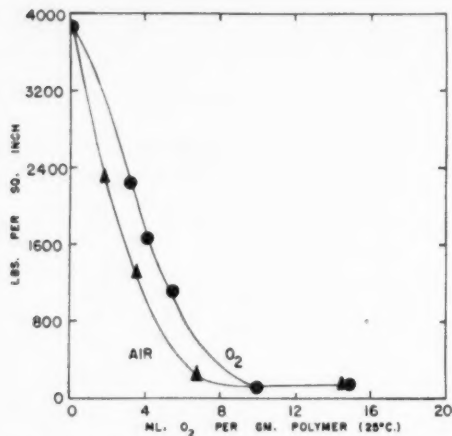


Fig. 10.—Tensile strength of uninhibited Hevea gum stock vs. oxygen absorption in air and oxygen. At 90° C, 760 mm.

The lower elongation and higher modulus and hardness values obtained in air for a given absorption of oxygen by the gum stock are in complete accord with the behavior observed with the black stocks. The effect of oxygen pressure on the nature of the aging obtained is actually more pronounced in the case of the gum stock. For example, the divergence of the curves for the 300

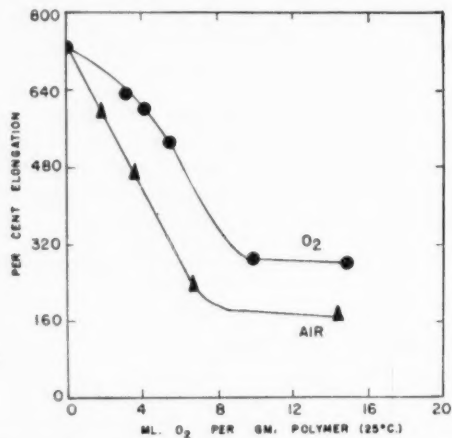


Fig. 11.—Ultimate elongation of uninhibited Hevea gum stock vs. oxygen absorption in air and oxygen. At 90° C, 760 mm.

per cent modulus observed by aging in air and oxygen is spectacular, as shown in Figure 12.

Thus it appears that an increase of the oxygen concentration in the aging atmosphere increases not only the rate of oxygen absorption but also the proportion of chain scission compared to cross linking for a given amount of oxygen absorbed. Aging in oxygen thus yields a softer stock with higher elongation

and lower modulus values than are obtained by aging in air. This is in agreement with work previously reported from this laboratory¹¹, where a stock aged in oxygen and in a circulating air oven at 100° C showed higher elongation and lower modulus values in oxygen for a given degradation of tensile strength.

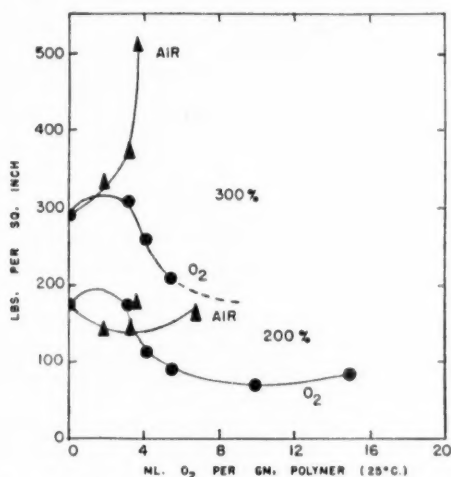


FIG. 12.—Moduli of uninhibited Hevea gum stock vs. oxygen absorption in air and oxygen. At 90° C, 760 mm.

GR-S black stock.—The effect of the oxygen pressure on the degradation of physical properties was apparent in the case of the GR-S black stock. The tensile strengths obtained after given oxygen absorptions from air were significantly lower than those for comparable absorptions from oxygen, as shown in Figure 14, the greatest effect appearing during the absorption of the first 4 to

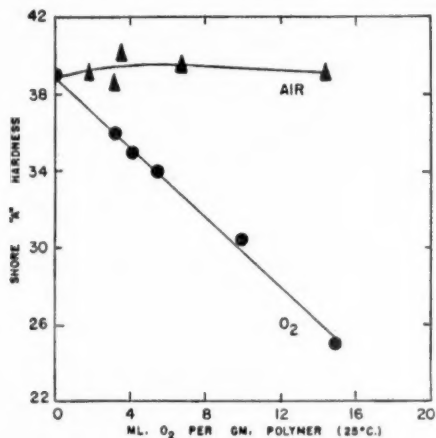


FIG. 13.—Hardness of uninhibited Hevea gum stock vs. oxygen absorption in air and oxygen. At 90° C, 760 mm.

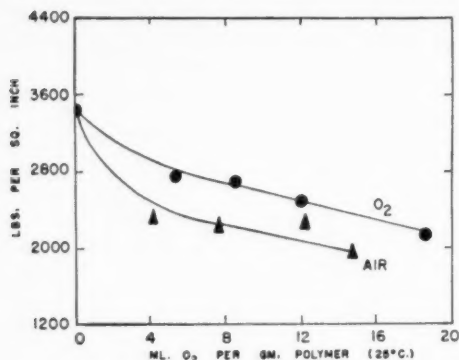


FIG. 14.—Tensile strength of GR-S black stock vs. oxygen absorption in air and oxygen. At 100° C, 760 mm.

5 cc. of oxygen per gram of polymer. Similarly, in Figure 15, the ultimate elongations after aging in air were much lower than in oxygen, and again the greatest difference occurred during the absorption of the first 4 to 5 cc. of oxygen.

Figure 16 and 17 show a higher modulus and greater hardness for samples aged in air than in oxygen. In all cases, the differences between properties in

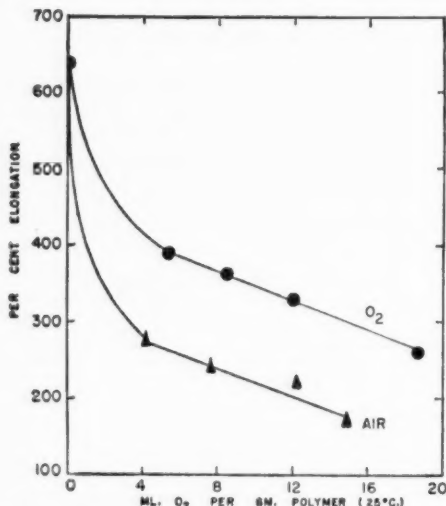


FIG. 15.—Ultimate elongation of GR-S black stock vs. oxygen absorption in air and oxygen. At 100° C, 760 mm.

air and in oxygen were much greater for the GR-S black stock than for the Hevea black stock, though in general the changes were in the same direction. The only exception is the tensile strength, in which case the Hevea stock exhibited little effect of oxygen concentration on the change produced by a given absorption of oxygen. The properties of the GR-S black stock varied so greatly

between oxygen and air aging that a stock aged a like time in air and oxygen would apparently be more deteriorated in air than in oxygen, even though it would have absorbed only about half as much oxygen. These relationships are shown in Table VI.

Comparison of GR-S and Hevea stocks.—These data tend to confirm the conclusion (noted previously in a study of the effect of temperature¹³ that GR-S is

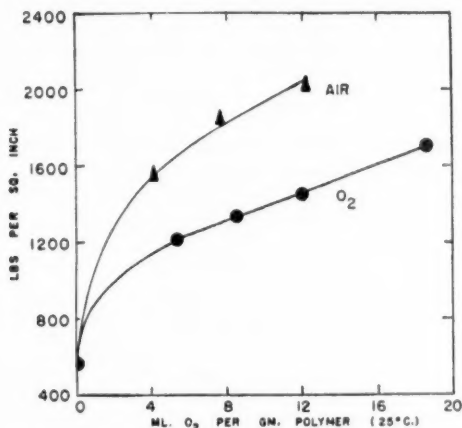


Fig. 16.—Modulus of GR-S black stock vs. oxygen absorption in air and oxygen. At 100° C, 760 mm.

much more subject to cross-linking than is natural rubber, and that natural rubber is more sensitive to chain scission. The comparatively large effect of the partial pressure of oxygen on the extent of tensile degradation in the case of GR-S is in sharp contrast to the negligible effect on the tensile degradation of the Hevea black stock for a given amount of oxygen absorbed. A similar

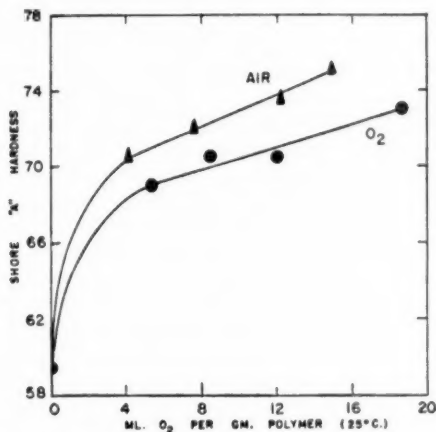


Fig. 17.—Hardness of GR-S black stock vs. oxygen absorption in air and oxygen. At 100° C, 760 mm.

anomalous behavior was noted in the prior study on the effect of temperature on the rate of deterioration of these stocks. This prior work¹³ showed that increased temperature increases the rate of deterioration of tensile strength for the Hevea stock, but decreases the rate of GR-S tensile degradation for a given oxygen absorption. Changes in other properties pointed to an increased rate of chain scission for both stocks with increased temperature. Similarly, the data for changes in other properties, as reported here, show evidence of increased chain scission with increased oxygen concentration. Thus it appears that the tensile strength of the Hevea stock is very sensitive to chain scission, but that in the case of GR-S, a higher ratio of chain scission to cross-linking may result in less deterioration of tensile strength for a given amount of oxygen absorbed!

The difference in the behavior of the Hevea and GR-S stock is probably inherent in the fundamental molecular structure. Natural rubber includes many molecules of very great chain length, and with little or no branching of the chain. The tensile strength of the rubber is believed to depend to a considerable degree

TABLE VI
PHYSICAL PROPERTIES OF GR-S BLACK STOCK AFTER EQUAL TIMES OF
AGING IN AIR AND OXYGEN AT 100° C, 760-MM. PRESSURE

Days of aging	Atmos- phere	cc. of O ₂ per gram polymer	Modulus 200%	Tensile strength (lb./sq. inch)	Elonga- tion (%)	Shore A hardness
0	—	—	560	3450	640	59.5
2	Oxygen	5.3	1220	2840	390	69.0
		3.7	1500	2500	290	70
3	Oxygen	7.7	1300	2700	370	70
		4.7	1600	2400	270	71
4	Oxygen	10.0	1380	2600	350	70.5
		5.7	1680	2350	260	71.0
6	Oxygen	16.4	1620	2280	290	72.5
		7.7	1820	2260	240	72

on the comparative ease with which these chains become aligned during elongation to form oriented crystalline micelles. A relatively small amount of oxygen may result in sufficient scission to reduce the average chain length drastically, and also introduce sufficient irregularity to contribute to the rapid degradation of the tensile strength.

The molecular chains of GR-S do not attain a length comparable to the longer natural rubber molecules, and the GR-S chains include considerable branching. Consequently, the GR-S molecules are difficult to align, and little tendency to crystalline orientation is present. Scission of an internal branch of the branched-chain molecule of GR-S will not reduce the over-all length of the molecule to the degree that would be expected in the case of a linear molecule of natural rubber. Furthermore, the cutting of some of the branches and cross-links of GR-S would tend to give molecules which could more easily enter into secondary valence associations, and thus a higher proportion of chain scission is not inconsistent with the observed higher tensile strength of GR-S aged in oxygen as compared to air.

The effects of chain scission and cross-linking tend to offset each other in part, and there must be an optimum ratio which results in a minimum change in properties. In the case of GR-S in air or oxygen at temperatures up to 100° C, cross-linking predominates, and the balanced ratio leading to minimum change must be at some higher temperature. Hevea rubber, on the other hand, exhibits a higher ratio of scission to cross-linking at the usual testing temperatures of 70° to 100° C, and the point of minimum change is, therefore, in the direction of room temperature.

It follows from the above discussion that the aging behavior of the Hevea black stock in air at normal storage temperatures should in general be better than that predicted by high temperature testing in oxygen. Conversely, the GR-S black stock would behave in the opposite manner and age more in air at normal storage temperature than would be expected on the basis of comparative tests in oxygen at a higher temperature. Data of the type presented here and in the references cited²⁰ will enable one to predict variations of this type, and thus improve the usefulness and reliability of the information obtained by accelerated aging tests.

CONCLUSIONS

The over-all rate of deterioration of physical properties increases with the oxygen concentration, as would be expected from the increased rate of oxygen absorption. The nature of the deterioration resulting from a given amount of oxygen absorbed is influenced also by changes in the partial pressure of oxygen in the aging atmosphere. It appears that chain scission is favored at higher oxygen concentrations, while cross-linking becomes of greater relative importance at lower oxygen concentrations. These data suggest that R· radicals are more effective than RO₂· radicals in reacting with double bonds to form cross-links.

Heat aging in the absence of oxygen, as observed by heating a vulcanizate in lamp-grade nitrogen, results in considerable stiffening, particularly in the case of a GR-S black stock. This effect is observed primarily in the first few hours of heating, and may account for some of the erratic behavior observed in the early stages of aging when changes in physical properties are compared on the basis of amount of oxygen absorbed.

Higher oxygen concentration brings about a more rapid oxidation, and also results in a higher proportion of chain scission compared to cross-linking for a given amount of oxygen absorbed. As tensile decay is the most evident sign of deterioration of Hevea stocks, it follows that the aging behavior of natural rubber in air at normal storage temperatures will be better than that predicted by high temperature testing in oxygen. In the case of GR-S stocks, on the other hand, oxidative hardening is the most serious result of aging, and consequently, the aging behavior of GR-S stocks in air at normal storage temperatures is poorer than would be expected on the basis of comparative tests in oxygen at higher temperatures.

ACKNOWLEDGMENT

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TECHNICALLY CLASSIFIED RUBBER—THE NON-RUBBER CONTENT AND THE MEASUREMENT OF CURE RATE *

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Since the volume application of Hevea rubber as a technical product, a system of market classification based on visual methods has been employed. This type of classification is not indicative of the technical properties or technical uniformity of the material. A recent paper by R. G. Newton, Phillpott, Harfield-Smith and Wren¹ sets forth the details of the variability of Malayan

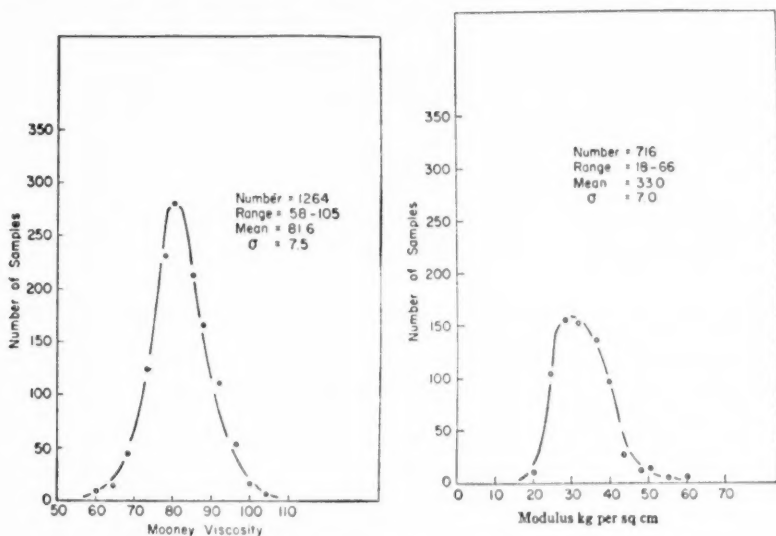


Fig. 1.—Survey of estate ribbed smoked sheet No. 1. Mooney viscosity of the raw rubber.

Fig. 2.—Survey of estate ribbed smoked sheet No. 1. Modulus at 600 per cent elongation (Schopper machine).

rubber from a statistical viewpoint. Figures 1 and 2 are taken from Newton's paper and indicate the distribution of two technologically important properties of rubber.

A system whereby information of a technical nature could be provided in addition to the market or visual classification was suggested by the French

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Delegation to the 1949 London Meeting of the International Rubber Study Group. When this additional information is provided, the rubber is called *technically classified rubber*. Natural rubber varies in its vulcanization and processibility characteristics, and the system as proposed attempts to classify rubber according to these characteristics. Users of natural rubber have become accustomed to technical variation in the material, and large consumers can overcome this by a blending procedure. However, this necessitates extra labor, scheduling difficulties are encountered, and routine testing of incoming shipments must be maintained at a high level. Many such operations could be materially reduced or eliminated if shipments of uniform and technically classified rubber could be obtained.

As a measure of the processability of the rubber, the Mooney viscosity (large rotor at 212° F, 4 minutes) is used while the rubber is classified according to rate of cure by the modulus obtained at 600 per cent elongation (dumbbell specimen) when cured 40 minutes at 127° C in the American Chemical Society's No. 1 formulation. Table I gives the criteria used to place individual lots of rubber into one of nine grades.

The present system of classification suffers from disadvantages, the most important of which are: (1) the initial Mooney viscosity gives no indication of

TABLE I
GRADING SCHEME

Processability		Vulcanization rate	
Mooney viscosity (ML for 4 min. at 212° F)	Sym- bol	Stress (modulus) at 600 per cent elongation in A.C.S. No. 1 mix after 40 min. at 127° C	Color of symbol
Less than 73	—	Less than 427 lb. per sq. in.	Red
73 to 87	O	427 to 711 lb. per sq. in.	Yellow
Greater than 87	X	Greater than 711 lb. per sq. in.	Blue

the rate at which a particular rubber breaks down on mastication; (2) it may not be possible to determine the rate of cure of any mix by a single cure, although more extensive work will be necessary to settle this point; (3) variations of moisture content of the mixed stock prior to curing give rise to variations in the curing characteristics.

This work was undertaken with the hope of determining the intrinsic differences among the various classes from a nonrubber hydrocarbon viewpoint. The cure rate of representative samples of all classes was investigated by several methods, and the data so obtained were examined with the results of the chemical (nonrubber) analyses in view. The chemical analyses performed are listed in the "Experimental Methods" section. The rate of cure was ascertained by means of: (1) the present ASTM method using the Mooney viscometer, (2) the conventional tension stress-strain testing method, (3) the National Bureau of Standards' strain test, (4) a new approach developed by Gee and Morrell², and (5) an application of the method of Gee to measurements made with the Mooney viscometer.

This work was carried out using a limited supply of each class of rubber and is not the result of many samples taken from many bales. This procedure had to be resorted to, since there was no source from which numerous samples could be drawn.

EXPERIMENTAL METHODS

Chemical analysis.

The following analyses were performed on the classified rubbers:

1. Percentage ash. Samples ashed 16 hours at 550° C.
2. Percentage nitrogen. Semimicro-Kjeldahl method.
3. Percentage acetone extract (ASTM D 297-50 T)⁵.
4. Percentage fatty acid (calculated as stearic acid). Ethanol-toluene azeotrope method originally developed for GR-S⁴.
5. pH of a slurry of the ash. Five cc. of water was added to the ash and the pH of this was measured.
6. pH of aqueous digest. Two grams of thinly sheeted rubber were digested at 90° C for 17 hours in 50 cc. of water and the pH of this digest was measured.
7. Hygroscopicity at room temperature. Approximately 1 to 2 grams of thinly sheeted (30 to 40 mils) rubber was dried over P₂O₅ to equilibrium. The dried samples were then placed in a 75 per cent relative humidity atmosphere and allowed to reach equilibrium. The increase in weight was measured.

Compounding.

The compounding was carried out according to the following scheme.

1. The A.C.S. No. 1 recipe was modified so as to give a constant fatty acid content in each mix. This fatty acid content was adjusted to 3.0 per cent (calculated as stearic acid) expressed on the total weight of the mix. The unmodified A.C.S. recipe is as follows:

Rubber	100.0
Zinc oxide	6.0
Stearic acid	0.5
Mercaptobenzothiazole	0.5
Sulfur	3.5

Chemical analysis showed that the red and yellow classes contained, as an average, 1.40 and 1.47 per cent, respectively, of fatty acid and that the blue class contained 2.0 per cent, all calculated as stearic acid. Therefore, 1.85, 1.85, and 1.37 parts per hundred of stearic acid were added to the red, yellow, and blue mixes, respectively. Such mixes, in which the fatty acid content was brought to an equal level, will be referred to as mix A.

2. Additional mixes were made, in which the A.C.S. No. 1 recipe was unaltered, and these will be referred to as mix B. All mixing was done on 6 by 12-inch mills at a mill temperature of 150° ± 5° F, following the mixing procedure called for with the A.C.S. No. 1 mix.

Physical testing.

The stocks after mixing were stored in an atmosphere of 50 per cent relative humidity at 77° F for a period of 7 days prior to curing, which was done at 260° ± 2° F. The testing was as follows on mix A:

1. Measurement of the scorching and cure rate characteristics of the stocks at 260° F by means of the Mooney viscometer (ASTM Method D 1077-49 T)⁵. Measurements of this type were made on samples conditioned for 7 days in atmospheres of 50 and 75 per cent relative humidity. The testing was carried out with the small rotor.

2. Tension stress-strain on 10, 20, 40, 80, and 160 minute cures, using the Standard Scott Tension Testing Machine (tested at 77° F) (ASTM Method D 412—51 T)⁶.

3. Strain measurements were made on each cure using the N.B.S. strain tester at a load of 100 lb. per sq. in. Three separate measurements were made for each cure.

On mix B the following testing was carried out.

1. Measurement of the modulus (force of retraction) at 100 per cent elongation with a modified triple beam balance. The load in kilograms was measured after the sample had been held at the desired elongation for 1 minute. The measurements were made at 25° C.

2. Ten viscosity-time curves were obtained with the Mooney viscometer for a typical red, yellow, and blue rubber; these were used for a statistical analysis.

Equilibrium swelling in benzene.

Equilibrium swelling of the cured vulcanizates of mix A was carried out in c.p. benzene at 25° ± 0.1° C. The swelling was carried out in darkness with 0.1 per cent of phenyl- β -naphthylamine added to the benzene. The volume fraction of polymer in the swollen vulcanizate was calculated by a technique similar to that described by Flory⁷.

DISCUSSION

Chemical analyses.

It has, of course, been known for many years that the amount and the nature of the nonrubber material present in Hevea rubber affects the curing characteristics and the resulting physical properties of the vulcanizate. This is

TABLE II
CHEMICAL ANALYSIS

	Ash (per cent)	Nitro- gen ^a (per cent)	Nitro- gen ^b (per cent)	Acetone extract (per cent)	Acidity ^c (per cent)	Fatty acid ^d (per cent)	pH of ash slurry ^e	pH of aqueous digest	Water sorbed from a 75 per cent rel- ative hu- midity atmos- phere (per cent)
Red { O X	0.18 0.17 0.23	0.37 0.37 0.33	0.38 0.36 0.35	2.34 2.66 3.32	0.037 0.042 0.043	— — —	8.2 7.5 8.0	4.3 5.0 5.1	0.09 0.09 0.08
Yellow { O X	0.24 0.20 0.22	0.38 0.39 0.39	0.35 0.38 0.37	2.86 3.20 3.12	0.040 0.042 0.038	— — —	8.0 7.9 8.0	5.7 4.8 4.9	0.10 0.13 0.09
Blue { O X	0.36 0.35 0.41	0.47 0.54 0.47	0.44 0.50 0.44	3.48 4.03 3.54	0.056 0.064 0.051	— — —	9.5 9.0 9.7	6.5 5.1 6.8	0.13 0.16 0.14
Average values									
Red	0.19	0.36	0.36	2.77	0.042	1.47	7.9	4.8	0.09
Yellow	0.22	0.39	0.37	3.06	0.040	1.40	8.0	5.1	0.11
Blue	0.37	0.49	0.46	3.68	0.057	2.00	9.4	6.1	0.14

^a Determined on unextracted samples.

^b Determined on acetone-extracted samples.

^c Acidity as milliequivalents per gram.

^d Calculated as stearic acid.

^e Ash digested in 5 cc. of water.

^f Two-gram samples digested 17 hours at 90° C in 50 cc. water.

true of both rubber-sulfur mixes and the so-called technical mixes which contain in addition to sulfur, zinc oxide, usually added fatty acid, and an organic accelerator. One might naturally expect that among the various classes of technically classified rubber, those with the higher rates of cure would contain increased amounts of nonrubber materials. The data presented in Table II and in Figures 3 and 4 indicate that this is evidently true. The data given in Figures 3 and 4 are averages of the three processability classes for each individual color class. According to the present scheme of classification, there are three classes for the cure rate, red (slow), yellow (medium), and blue (fast).

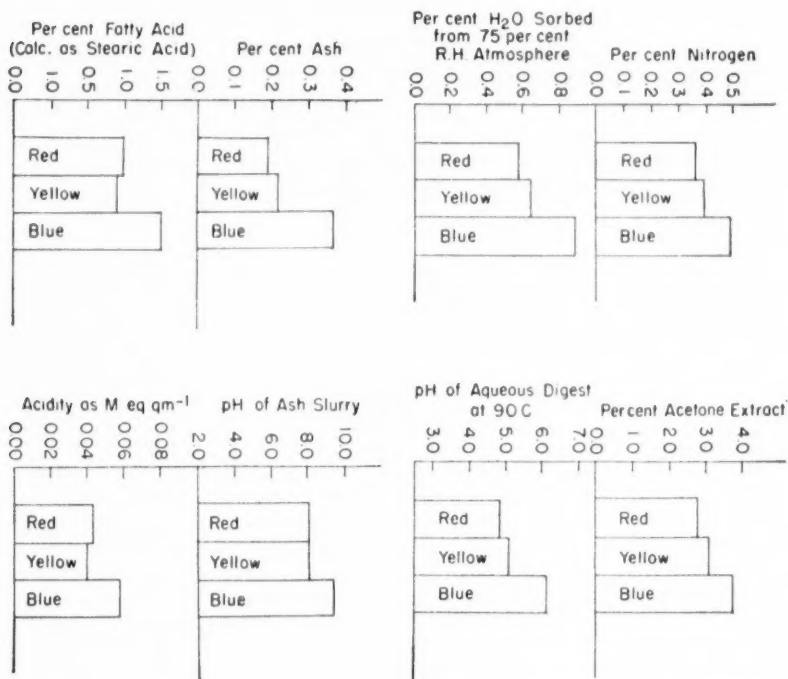


FIG. 3.—Nonrubber content of the various color classifications of technically classified rubber.
FIG. 4.—Nonrubber content of the various color classifications of technically classified rubber.

Blue rubber contains greater amounts of fatty acid, ash, and nitrogen than the yellow and red rubbers; in addition, the acetone extract, the pH of a slurry of the ash, and the pH of the aqueous digest are greater. The amount of moisture that would be taken up under atmospheric conditions is slightly different for each color class, the blue class having a greater affinity for moisture.

The data of Table II indicate that the rubbers do genuinely differ from each other, blue rubber containing the highest amount of nonrubber material, yellow rubber lesser amounts, and the red rubber the least. With this in mind, the cure rate data of the A.C.S. No. 1 type mixes of each of the classified rubbers can be examined.

TABLE III
 MOONEY CURE DATA

		Scorch time ^a (T_{mv+5}) (min.)		Cure rate, ^b R_{25} Mooney units per min.	
		I	II	I	II
Red	—	11.9	11.2	6.3	6.3
	O	16.8	11.1	5.3	5.4
	X	9.3	7.7	7.9	7.5
Yellow	—	8.7	7.7	8.3	8.6
	O	12.0	10.0	6.5	6.5
	X	9.6	7.8	8.1	8.6
Blue	—	4.8	3.7	10.9	10.0
	O	5.7	4.7	11.4	11.9
	X	4.0	3.5	11.4	11.9

Notes:

I—Conditioned 7 days at 50 per cent relative humidity.

II—Conditioned 7 days at 75 per cent relative humidity.

^a Corrected for thermal lag.^b R_{25} is the average rate of increase of viscosity over the range T_{mv+5} to T_{mv+25} .*Rate of cure.*

The Mooney viscometer has been used quite widely to determine the scorching characteristics of typical rubber mixes at curing temperatures. It has also been adapted by Shearer, Juve, and Musch⁸ for the measurement of the cure rate of typical rubber mixes. It has been the practice in these laboratories to define the scorch time as the total elapsed time necessary to reach the minimum viscosity and increase five units of viscosity above the minimum. This is designated T_{mv+5} . The cure rate is arbitrarily defined as $25/t$, where t is the time to increase 25 units of viscosity above the point T_{mv+5} .

The behavior of the nine classes compounded into mix A when subjected to such testing is shown in Table III and Figure 5. The scorch times decrease in the order red-yellow-blue, while the cure rates increase in the same order. When the moisture content of the stock is altered, the scorch time is also altered, higher moisture contents favoring a reduced or shorter scorch time. The cure rate as measured by the previously described method does not reflect the difference in moisture content, as does the scorch time, although there is a slight trend toward higher rates at the higher moisture level as determined by this particular method. It has been previously shown that the A.C.S. No. 1 mix is sensitive to moisture in regard to rate of cure. It is evident from these

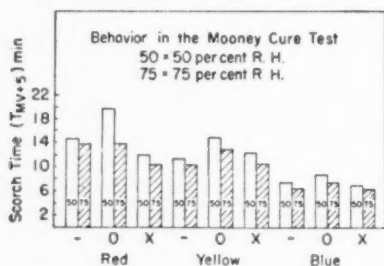


Fig. 5.—Effect of varying moisture content of the A.C.S. mixes on the time to scorch.

TABLE IV
TENSION STRESS-STRAIN PROPERTIES
Vulcanizates cured at 260° F (127 C). Individual values reported for M600,
tensile strength, and per cent *E* are the mean of five measurements

Cure time (min.)	M600 ^a			M600			M600		
	Tensile strength (lb. per sq. in.)			Tensile strength (lb. per sq. in.)			Tensile strength (lb. per sq. in.)		
	Red—			Red O			Red X		
10	—	380	760	—	—	—	—	465	860
20	300	1750	905	200	1130	860	395	2410	885
40	595	2455	825	485	2595	845	660	2895	820
	Yellow—			Yellow O			Yellow X		
10	—	390	875	—	330	770	165	1105	900
20	460	2440	860	245	1470	885	525	2540	820
40	740	3185	810	600	2555	800	815	3040	780
	Blue—			Blue O			Blue X		
10	530	2095	845	585	1975	780	600	2580	810
20	1040	3345	800	1060	3065	765	945	3370	800
40	1255	3930	780	1435	3840	765	1390	4100	785

^a Modulus as 600 per cent elongation.

data that for the successful evaluation of rate of cure the moisture content of the mix should be adjusted to some fixed level. This would be particularly important in any scheme where cure rate was measured during the early stages of cure, as with the Mooney viscometer.

The stress-strain data for the nine vulcanizates of mix A are given in Table IV. Examination of these data show qualitatively the same trend encountered

TABLE V
STRAIN MEASUREMENTS

Cure time (260° F) (min.)	Strain (per cent ^a)		
	Red—	Red O	Red X
10	488	^b	^c
20	233	^b	185
40	148	165	120
80	103	108	88
160	87	89	80
	Yellow—	Yellow O	Yellow X
10	^c	^d	288
20	161	252	138
40	111	145	109
80	83	101	84
160	79	83	76
	Blue—	Blue O	Blue X
10	225	141	130
20	102	94	91
40	82	78	80
80	71	67	72
160	70	67	69

^a Mean of three measurements made at 100 psi.

^b Defective sample.

^c Creep too high for strain measurement to be significant.

^d Sample too porous to test.

in the tests conducted with the Mooney viscometer. The fast rate of cure of the blue rubber is clearly indicated by the modulus at 20 minutes of cure.

The data obtained from the strain measurements on the nine classes (in mix A) are shown in Table V. Here again the behavior as exemplified in the stress-strain measurements is evident, blue rubber being much faster in rate of cure than the yellow and red classes. Roth and Stiehler⁹, in their paper on the use of the strain test, state that a rectangular hyperbola is obtained from a plot of strain *vs.* time of cure. One of the three vulcanization parameters obtained from their treatment is the intercept of the strain axis asymptote on the time axis, designated as t_0 and referred to as the time of incipient cure or the scorch time. It was hoped that a relationship between the scorch time obtained with the Mooney viscometer and the scorch time t_0 of the hyperbola could be found. However, the scorch times from the strain-time curves were very erratic and were not related to those found with the viscometer. The exact reason for this lack of correlation is not known. Most of the work described by Roth and Stiehler in their original paper was done using GR-S carbon black mixes, and very little comment is made concerning gum stocks. The degree to which their strain-time data are approximated by a hyperbola may be characteristic of carbon black mixes.

The vulcanizates of mix A were characterized as to state of cure by the number average molecular weight between cross-links, M_c , which was determined by equilibrium swelling in benzene. From the work of Flory and Rehner¹⁰ a relation between M_c , the volume fraction of polymer in the swollen gel (vulcanizate), and the molar volume of the swelling liquid has been developed.

$$M_c = \frac{-\rho V_1 V_2^{\frac{1}{2}}}{[\ln(1 - V_2) + V_2 - \mu V_2^2]} \quad (1)$$

where:

M_c = number average chain molecular weight.

ρ = density of polymer.

V_1 = molar volume of swelling liquid.

V_2 = volume fraction of polymer.

μ = a polymer-solvent interaction constant ($\mu = 0.39$ for rubber-benzene)¹¹.

M_c , of course, decreases as the number of cross-links in the network increases. The relationship between M_c , the class of rubber, and time of cure is shown in Table VIII.

It has been the most common practice of rubber technologists to measure the cure rate of any given mix by the inverse of the time necessary to reach the optimum or some given modulus. While this has practical value, the technologically important problem of rate of cure surely deserves a more quantitative treatment. Such a treatment has been made by Gee and Morrell³. The considerations that he has given to this problem will now be briefly mentioned.

To measure accurately the rate of cure, some parameter must be found which will assess the state of cure, and the time variation of this parameter can then be examined. Gee found that a function of the state of cure could be defined as follows:

$$\phi(\text{state of cure}) = f + \phi'(M) + \text{constant} \quad (2)$$

where:

f = modulus (force of retraction at 100 per cent elongation) and
 $\phi'(M)$ = a function of the linear molecular weight of the rubber before vulcanization.

ϕ (state of cure) is defined by the parameter M_c (strictly the true M_c) while $\phi'(M)$ is defined by the Mooney viscosity V_c of the compounded mix before vulcanization (large rotor at 100 C). In terms of M_c and V_c , Equation 2 becomes:

$$\frac{3.27 \times 10^5}{M_c} = f + \frac{105.0}{V_c + 18.7} - 1.31 \quad (3)$$

$3.27 \times 10^5 M_c^{-1}$ has the dimensions of modulus (force per unit area), and can be set equal to a quantity X for convenience. X is equal to a measured modulus f , corrected for the contribution which is independent of cure, that is, the term containing V_c . The relation connecting the linear molecular weight (osmotic molecular weight) and the Mooney viscosity was found by Gee and coworkers to be:

$$M = 6.23(V_c + 18.7)10^5 \quad (4)$$

The M_c as defined in Equation 3 is the true or chemical molecular weight per chain. It is the average molecular weight between (chemical)-sulfur cross-links, and does not include those entanglement constrictions that behave from an elastic viewpoint as if they were true cross-links. Modulus-time curves for many types of mixes can best be described by the following equation:

$$X = X_\infty(1 - e^{-kt}) \quad (5)$$

where:

X = (as defined above), kilograms per square centimeter.
 k = a rate constant describing the time dependence of X (min^{-1}).
 X_∞ = a constant, the value of X at infinite time of cure.
 t = time (min.).

Once X_∞ is known, the constant k then describes the time behavior of X . This constant may be termed the vulcanization rate constant, its value reflecting the rate of cure of any particular mix. For Equation 5 to be strictly valid, no reversion should take place; however, it may still be used with effectiveness if the reversion is not pronounced. The effects of reversion at moderate curing temperatures are all but negligible in the initial stages of cure, and it is the initial portion of the modulus-time curve that best typifies the modulus-time behavior. In terms of the measured f , Equation 5 becomes:

$$f = f_\infty - (f_\infty - f_0)e^{-kt} \quad (6)$$

since $X = f - f_0$ and $X_\infty = f_\infty - f_0$ where $f_0 = 1.31 - \frac{V_c + 18.7}{105.0}$. The parameter f_0 is obtained from Equation 3 when $\frac{3.27 \times 10^5}{M_c}$ is set equal to zero, that is, at zero time. Then, according to Gee:

$$f = f_0 = 1.31 - \frac{105.0}{V_c + 18.7} \quad (7)$$

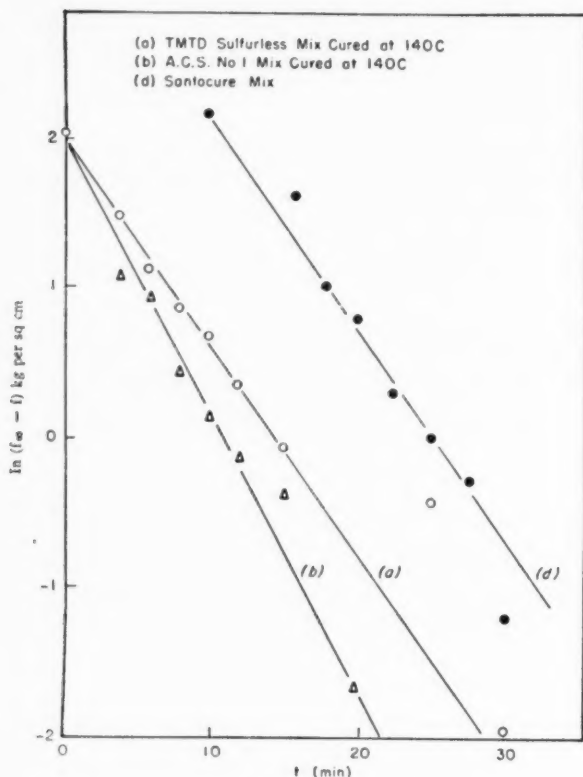


FIG. 6.—Plots of $\ln(f_\infty - f)$ vs. t for typical gum mixes of natural rubber (data of Gee).

The algebraic value of f_0 is a measure of the molecular weight of the unlinked rubber molecules before vulcanization, and f_0 is a constant for any particular mix.

Equation 6 may be set into logarithmic form.

$$\ln(f_\infty - f) = -kt + \ln(f_\infty - f_0) \quad (8)$$

Plots of $\ln(f_\infty - f)$ vs. t will enable k to be calculated. Figure 6 shows results that were obtained by Gee from vulcanizates of typical gum mixes of natural rubber. Figure 7 shows a typical plot that was obtained from the vulcanizates of mix A. The values of f for these vulcanizates were obtained from swelling measurements by means of the following empirical equation that was derived by Gee and coworkers.

$$f = 3.6 \times 10^4 \frac{1}{M'_c} + 1.31 \quad (9)$$

In this equation, M'_c is the effective chain molecular weight which results from the aforementioned network entanglements ($M_c > M'_c$). The constant 1.31

arises from an empirical equation relating stress and strain in gum vulcanizates of natural rubber at moderate elongations. Table VI gives the values of the parameters found for mix A along with those found by Gee for the typical mixes indicated in Figure 6. With only one exception the values of k are grouped together, as one would expect, for the red, yellow, and blue classes. The values of the average or mean k for each class seem to indicate that the cure rates of the red and yellow mixes are very close. This type of behavior parallels that found in the chemical analysis data where, from a nonrubber viewpoint, the red and yellow classes were very nearly alike.

Figure 8 is a plot of the rate of cure, determined by the empirical method with the Mooney viscometer, *vs.* the rate constant, k , as determined by Gee's equation. The general spread of the points indicates that there is a qualitative agreement between the two methods and suggests that the possibility of utilizing the Mooney viscometer for the measurement of cure rate in a less empirical manner be investigated. The developments that have been made along these lines will now be described.

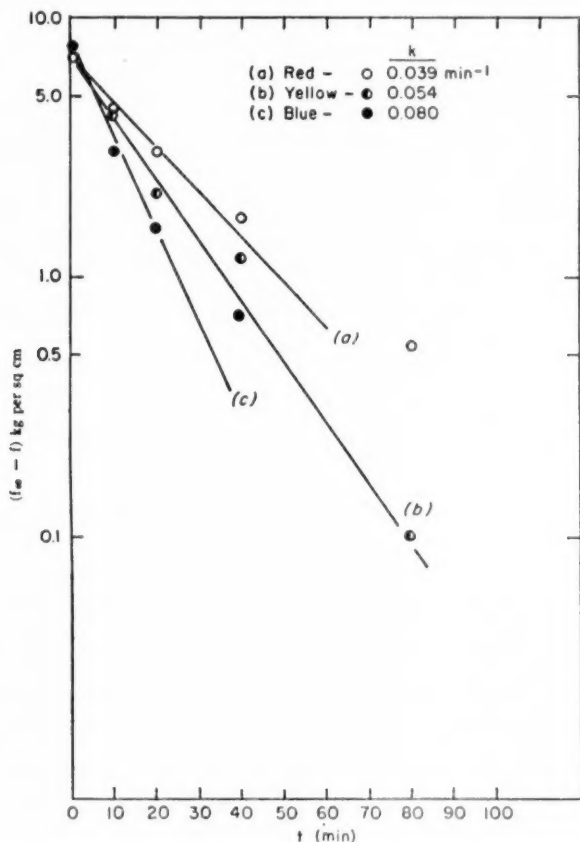


Fig. 7.—Plots of $\ln(f_{\infty} - f)$ vs. t for the gum mixes red—, yellow—, blue— (mix A).

Viscosity-time curves of vulcanizable mixes (in the Mooney viscometer) are characterized by three separate regions: (1) the early part of the curve, where viscosity is decreasing with time due to the gradual attainment of the impressed temperature; (2) a central region where viscosity is more or less independent of time, and (3) the region where the viscosity begins to increase with time due to the curing reactions. The character of the entire curve depends on temperature, degree of breakdown, and concentration and nature of the nonrubber hydrocarbon contents of the mix. Previously it had not been known what processes were responsible for the increases of viscosity in these early stages of cure. On a molecular basis, two possible causes for the initial viscosity increase can be postulated: (1) linkage of linear molecules to form still longer linear molecules and thereby increase the viscosity, or (2) the formation of a network. It has been found that almost the entire contribution to viscosity increase is the formation of a network.

TABLE VI
CURE RATE CONSTANTS
Data of Gee

Type mix	$-f_0$	f_∞ (kg. per sq. cm.)	Vulcanization temperature (deg. Cent.)	k (min ⁻¹)
A.C.S. No. 1	0.20	7.20	140	0.182
Tetramethylthiuram disulfide (no sulfur)	0.22	7.18	120	0.062
Santocure	0.39	7.20	140	0.138
	0.34	8.25	140	0.140

Data of mix A. Vulcanization temperature 127° C

Grade	$-f_0$	f_∞ (kg. per sq. cm.)	k (min ⁻¹)	Mean k (min ⁻¹)
Red { —	0.24	6.93	0.039	0.042
Red { O	0.31	6.68	0.038	
Red { X	0.31	6.86	0.049	
Yellow { —	0.31	6.84	0.054	0.050
Yellow { O	0.42	6.64	0.042	
Yellow { X	0.18	7.23	0.054	
Blue { —	0.13	7.48	0.080	0.084
Blue { O	0.18	7.59	0.085	
Blue { X	0.18	7.59	0.088	

This was determined by the following procedure. Samples of a typical mercaptobenzothiazole (MBT) mix were inserted into the viscometer at 260° F and, after the 1-minute warm-up, shearing was begun. After viscosity increases of 10, 20, and 30 units (one sample for each increase), each sample was quickly removed and plunged into ice water. After drying, representative sections were taken and swollen in benzene and the modulus f was calculated. From this a curve relating ΔV_c , the viscosity increase, and f could be constructed. This was done, and a linear relationship between the two variables was found over the range of viscosity increase that was investigated. The equation of the line shown in Figure 9 is:

$$f = 0.0464\Delta V_c + 1.31 \text{ (in kg. per sq. cm.)} \quad (10)$$

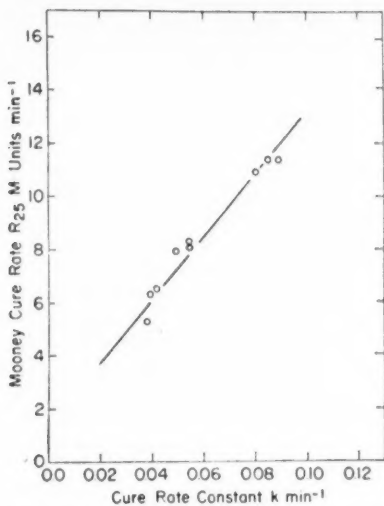


Fig. 8.—Mooney cure rate (R_{25}) vs. cure rate constant k (mix A).

With this relationship it should be possible to measure the time increase of modulus over the first several minutes of the rising viscosity curve. Once the value of f_{∞} , the modulus at infinite time of cure, is known, it is possible to construct curves of $\ln(f_{\infty} - f)$ vs. time, and from these curves a rate constant can be calculated. Barring any unforeseen difficulties, the rate constant calculated in this manner should be a reliable estimate of the rate constant calculated from

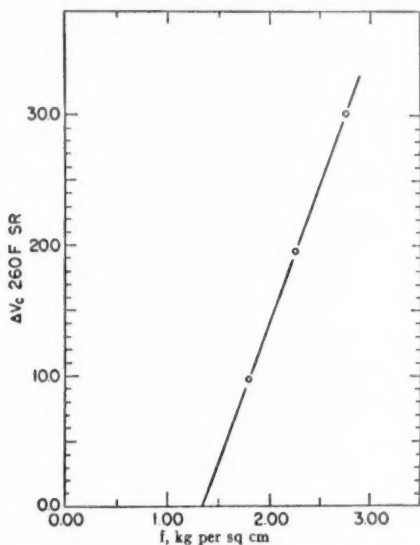


Fig. 9.—Viscosity increase ΔV_c (small rotor at 260° F) vs. modulus f .

actual modulus measurements on press cures. Preliminary data were obtained to test this and are given in Table VII. The agreement between the two methods can be considered satisfactory. Some experimental features are worth mentioning. The press cures were made in a mold whose geometry approximated that of the viscometer chamber insofar as rate of attainment of impressed temperature is concerned. Since there is a definite thermal lag in a sample as thick as that in the Mooney viscometer, corrections for this thermal lag must be made. An approximate method for doing this has been used in these laboratories for the past several years. It consists essentially of using a correction table constructed from temperature-time curves, with the temperature coefficient of cure assumed to be 2.0 for a 10° C rise. The temperature scale values increase in a geometric manner, cure doubling every 10° C. The area under any temperature-time curve is a measure of the extent of cure in arbitrary units. From these curves a correction table can be drawn up giving a corrected time of cure for any actual time in the viscometer chamber, for example, 10 minutes gives a corrected time of 7.3 minutes. Corrections of this nature were applied to both the press cures and the viscometer data in making this preliminary test. The success of this initial trial prompted additional work

TABLE VII
COMPARISON OF RATE CONSTANTS OBTAINED FROM MOONEY
VISCOMETER AND FROM PRESS CURES IN TRIAL 1.

Rubber	Rate constant from press cures (min ⁻¹)	Rate constant from viscometer data (min ⁻¹)
Red	0.041	0.038
Yellow	0.051	0.048
Blue	0.092	0.095

to further substantiate the utility of this method and to investigate the problem in a statistical manner.

Statistical analysis.

Mixes based on rubbers from the three cure rate classifications of red, yellow, and blue were made (mix B), and from each mix ten viscosity-time curves were obtained at 260° F. From the same mixes, press cures were made at selected intervals of time, and ten modulus measurements were made at each cure.

In calculating the cure rate constant with the viscometer, the following simplification of the equations of Gee may be made:

$$k = \frac{1}{t} \ln \frac{(f_{\infty} - f_0)}{(f_{\infty} - f)} \quad (11)$$

Since $f = 0.0464 \Delta V_c + 1.31$, this may be inserted into Equation 11. A further simplification can be made by adopting a constant value for ΔV_c . When this is done, the time to attain this value in any given viscosity-time curve can be measured. A value of $\Delta V_c = 15.0$ is arbitrarily adopted, and when this is inserted into Equation 11 it becomes:

$$k = \frac{1}{t} \ln \frac{(f_{\infty} - f_0)}{(f_{\infty} - 2.01)} \quad (12)$$

The knowledge of f_{∞} and f_0 now enables k to be calculated when the corrected time necessary to produce a viscosity rise of 15.0 units is known. A comparison

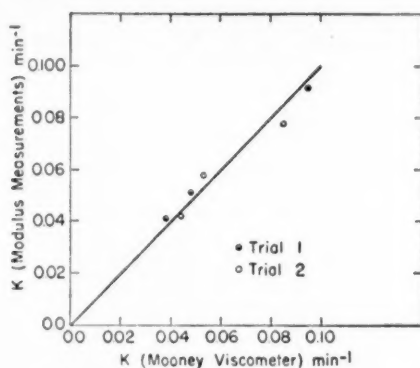


Fig. 10.—Comparison of cure rate constant by modulus measurements with the cure rate constant obtained with the Mooney viscometer.

between the rate constants found with the viscometer and those obtained from the actual modulus measurements is made in Figure 10. These points are designated as Trial 2. Those points designated as Trial 1 are the preliminary tests previously mentioned. The line drawn has unit slope and, of course, corresponds to exact correlation between the two methods. Although there is some degree of scatter of the points, the results of both trials can be considered as satisfactory.

To ascertain whether the cure rates of these samples are genuinely different from each other, the data of the replicate determinations made with the viscometer were subjected to variance analysis. Table IX gives the result of this analysis, and it can be readily seen that the three samples of rubber—that is, the red, yellow, and blue mixes—are significantly different in their rate of cure. To obtain an estimate of the variation of some typical viscosity-time curve

TABLE VIII
SWELLING DATA

Time of cure (260° F) (min.)	V_2 M_2		V_2 M_2		V_2 M_2	
	Red—		Red O		Red X	
20	0.134	14 300	0.122	17 400	0.148	11 300
80	0.185	7 100	0.182	7 800	0.193	6 800
	Yellow—		Yellow O		Yellow X	
20	0.156	10 400	0.127	15 600	0.164	9 600
80	0.195	6 600	0.183	7 500	0.196	6 500
	Blue—		Blue O		Blue X	
20	0.182	7 800	0.183	7 300	0.183	7 300
80	0.204	5 900	0.206	5 800	0.206	5 800

TABLE IX
ANALYSIS OF VARIANCE
(Cure rate constants for mix B)

Source of variation	Degrees of freedom	Variance
Between samples	2	42.6×10^{-4}
Within samples	24	18.4×10^{-6}

TABLE X
VARIATION OF SOME PARAMETERS OF VISCOSITY-TIME CURVES

	Minimum viscosity of small rotor at 260° F	Scorch time t_{mv+2} (min.)	Cure rate constant k (min ⁻¹)
Mean	26.3	4.3	0.053
Range	27.5 to 25.0	4.9 to 3.7	0.065 to 0.047
Number of tests	19	18	19
Variance	0.593	0.125	28.8×10^{-6}

parameters, a 10-week study with the Mooney viscometer was made. This consisted of two test per week made on a master mix from a homogenous lot of blended rubber. The mixing was done prior to the beginning of testing, and the samples were stored at 0° C until one week before their scheduled testing. One week before testing, the samples were placed in an atmosphere of controlled humidity and temperature (50 per cent relative humidity and 77° F) and kept there until tested. Storage at 0° C was employed to prevent any possible pre-

TABLE XI
CONVERSION OF MOONEY VISCOSITY, SMALL ROTOR, 260° F
TO MOONEY VISCOSITY, LARGE ROTOR, 212° F

$V_{min.}$ (260° F, small rotor)	$V_{min.}$ (212° F, large rotor)
10	25
12	30
14	34
16	39
18	43
20	46
22	49
24	52
26	56
28	60
30	64
32	67
34	70
36	73
38	76
40	79

mature cure or scorching of the samples during the ten weeks. Table X gives some of the mean values of these parameters with their associated ranges and variances.

Further utilization of the viscometer.

The preceding has shown that the Mooney viscometer is capable of reliably estimating the cure rate constant of a MBT mix if the parameters f_0 and f_∞ are known. If knowledge of one or both of these quantities could be furnished by the viscometer during the short-time test at the curing temperature, it would eliminate the necessity of another test to determine either f_0 or f_∞ . Considering f_∞ there is little chance that this can be accurately predicted from any type of viscometer data; however, f_0 , whose magnitude is governed by V_c (at 212° F),

might possibly be estimated from the viscosity-time curve. The minimum viscosity in any viscosity-time curve should be some function of the viscosity at 212° F, V_c . Ideally, if the test for the calculation of the rate constant continued for a sufficient time so that thermal equilibrium was reached (approximately 8 minutes) and provided no cross-linking took place during the 8 minutes, the 8-minute value of viscosity or the minimum value should be quantitatively related to the value of V_c at 212° F. If such a relationship could be found, then f_0 could also be evaluated.

Unpublished work in these laboratories has shown that the Mooney viscosity for any given viscosity level can be fairly well represented as a function of temperature by an equation of the form: $\log V = C_1(1/T) + C_2$ (V = viscosity, T = absolute temperature). The constants C_1 and C_2 vary with the viscosity level. This variation can, nevertheless, be taken into account and, if sufficient data are available, a table can be constructed to give a viscosity at one temperature T_1 when it is measured at another temperature T_2 . Table XI is such a table. One further correction that must be made is the correction from the small rotor viscosity to the large rotor viscosity. It has been found that 1.8

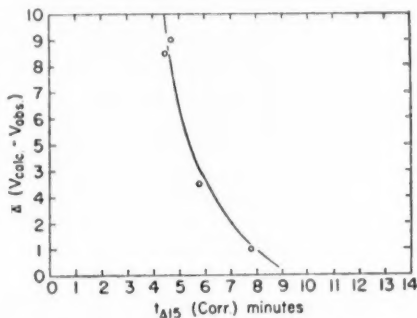


Fig. 11.—Plot of Δ (calculated viscosity at 212° F minus observed viscosity at 212° F) vs. time to increase 15 Mooney units, $t_{\Delta 15}$.

is the ratio between the large rotor and small rotor viscosities in the region of 260° F. This correction has been incorporated into Table XI and the value of V_c (large rotor at 212° F) may be found from the minimum viscosity, small rotor at 260° F.

The ideal case, as mentioned above will not exist, since in most instances appreciable cross-linking will occur during the first 8 minutes of heating at 260° F. When this is the case, the calculated value of the viscosity at 212° F based on the minimum viscosity at 260° F will be in error. This may be corrected to a first approximation by the use of a curve as shown in Figure 11. In this plot Δ represents the difference between a calculated viscosity at 212° F and a measured viscosity, both on the same mix. The quantity $t_{\Delta 15}$ is the time necessary to increase the viscosity 15 units ($\Delta V_c = 15$). At small values of $t_{\Delta 15}$ the deviation of the calculated viscosity from the measured one is large; at higher values of $t_{\Delta 15}$ (slower cure rate) the deviation is less serious and it should be for practical purposes almost nonexistent at values of $t_{\Delta 15}$ of 10 or more. The curve of Figure 11 is intended merely to show the general relationship between Δ and $t_{\Delta 15}$. More extensive data would be needed to place quantitative significance on this particular curve.

It has now been shown that the Mooney viscometer is capable of providing apparently reliable values of f and f_0 during the first several minutes of cure and that these can be used, when f_∞ is known, to calculate the cure rate constant. The inability of the viscometer to provide a value of f_∞ makes it necessary to adopt one of the following three procedures in order to calculate the rate constant.

1. Measure the modulus at some long time of cure at 260° F (160 minutes) and assume this to be equivalent to f_∞ .
2. Measure the modulus obtained from a cure for a shorter time at a higher temperature—for example 45 to 55 minutes at 280° to 285° F and assume this to be equal to f_∞ .
3. Assume some average value for f_∞ based on the results of many tests.

The degree of uncertainty of the value f_∞ increases from procedure 1 to procedure 3, while the time expenditure to obtain the desired result decreases in the same order. If the viscometer is to be used as an instrument to classify rubber according to rate of cure, any one of these may be adopted depending on the accuracy desired. If only approximate classification is sought, an even simpler modification can be arrived at, merely the time necessary to increase a given number of viscosity units. The degree of accuracy necessary will therefore dictate the method to be chosen.

After examining the paper of Gee and coworkers, in which the theory defining the rate constant k is set forth, the critical reader will detect a degree of contradiction between some of the features of the work reported here and the exposition of Gee and coworkers. Specifically, it is very surprising that the relationship between ΔV_c and f is linear. If this is true, it means that a full (overall time values) modulus-time curve is sigmoidal and that the negative modulus values of Gee are without foundation. It is not the purpose of this investigation to consider the theoretical aspect of this, even though it tends to question the agreement between the two methods for determining rate constants. The degree of confidence in using the viscometer to determine cure rate constants is justified solely on the basis of experiment.

This investigation was undertaken in an exploratory manner, and the results, as is readily apparent, are not in final form. It is felt nevertheless that useful information has been found and that it should prove valuable to those interested in the technical classification of natural rubber. It should be mentioned that the general problem of determining the rate of cure is in a somewhat intractable state, and a complete and critical appraisal of all schemes naturally requires the accumulation of much experimental data.

SUMMARY

The nonrubber content of typical samples of all grades of technically classified rubber has been determined. It is found that the nonrubber content increases in the order: red, yellow, and blue. The chemical analyses performed to determine the nonrubber content were as follows: per cent ash, per cent nitrogen, per cent acetone extract, and per cent fatty acid. The pH of both a slurry of the ash and the aqueous digest indicates that blue rubber is more basic in these respects than are red and yellow rubbers.

The measurement of the cure rate of these samples of technically classified rubber has been carried out by means of (1) conventional stress-strain testing, (2) the present ASTM method utilizing the Mooney viscometer, (3) the Na-

tional Bureau of Standards strain test, (4) a new and more quantitative approach developed by Gee and coworkers, and (5) a utilization of the Mooney viscometer to determine two of the parameters of Gee's equation which gives the time dependence of modulus. All of these methods place the rubbers in the same relative order.

The use of the viscometer to determine two of the parameters of Gee's equation was prompted by the degree of correlation between the rate parameter obtained with the present ASTM method and the rate constant k calculated by Gee's methods. As a result of a preliminary investigation as to the causes of viscosity increases at curing temperatures, it was found that, within limits of experimental error, all of the viscosity increase is due to the formation of a cross-linked network, with a linear relationship existing between viscosity increase ΔV_c and modulus (at 100 per cent elongation) f . The results of a comparison of the rate constants obtained by the viscometer and by Gee's method indicate that for MBT mixes at 260° F there is good agreement between the methods.

Statistical analysis shows that the samples employed for this study are significantly different in their rate of cure. The variance, range, and mean of some of the parameters obtained with the viscometer over a 10-week period are also given.

It is suggested that the Mooney viscometer be employed to classify natural rubber according to its cure rate. If this is done, it will be necessary to define the degree of accuracy desired. To determine accurately the cure rate, it is necessary that the viscometer be used in conjunction with a press cure for the estimation of the parameter f_∞ . If it is not feasible to carry out press cures, an average value for f_∞ can be assumed, and then only a short time test with the viscometer is required.

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THE VULCANIZATION OF THICK SHEETS OF RUBBER *

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INTRODUCTION

Articles of soft rubber are normally vulcanized by heating a mixture of unvulcanized rubber, fillers, accelerator and sulfur at a moderately high temperature for a certain time in a heated mold which heats both sides of the sheet. At the conclusion of the fixed period of time, the article is taken from the mold and is allowed to cool to the temperature of its surroundings.

Vulcanization takes place during each of three distinct phases.

Phase 1. The unvulcanized mix is heated to a particular temperature.

Phase 2. The mix is maintained at this temperature.

Phase 3. The vulcanized article is removed from the mold and is allowed to cool to the temperature of its surroundings.

In Great Britain the properties of the vulcanized mix are usually determined by tests on sheets of rubber, $10 \times 10 \times \frac{1}{16}$ inches which are vulcanized for various times at a suitable temperature. The best time of vulcanization is decided by considering the results of the tests. Since rubber is a poor conductor of heat, the properties of sheets $\frac{1}{16}$ inch thick differ from those of thicker sheets which are undervulcanized when they are given the same time of vulcanization.

This investigation was made in order to determine: (1) the extra time necessary to give the major part of a thick sheet the same amount of vulcanization as a $\frac{1}{16}$ -inch sheet, and (2) the uniformity of vulcanization of sheets throughout their thickness.

Qualitative recommendations for a longer period of vulcanization for thick articles have been made. A quantitative recommendation¹, obviously obtained from actual practice, for the vulcanization of a repair in a belt carcass has been given.

The method of investigation, the theory of the method and its application to sheets of $\frac{1}{16}$, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ and 1 inch thickness are described in this paper.

METHOD OF INVESTIGATION

The amount of vulcanization given to a sheet of rubber depends on the temperature, the amount of vulcanization per unit time, and the time of vulcanization. Phases 1 and 3 of vulcanization are divided into periods of time which are small compared with the total time of vulcanization. The amounts of vulcanization during the whole of phases 1 and 3 are related to the temperatures obtained during the small periods of time. The amount of vulcanization during any small period of time is the intensity of vulcanization at the temperature of a fixed plane in the sheet of rubber multiplied by the length of the period; an

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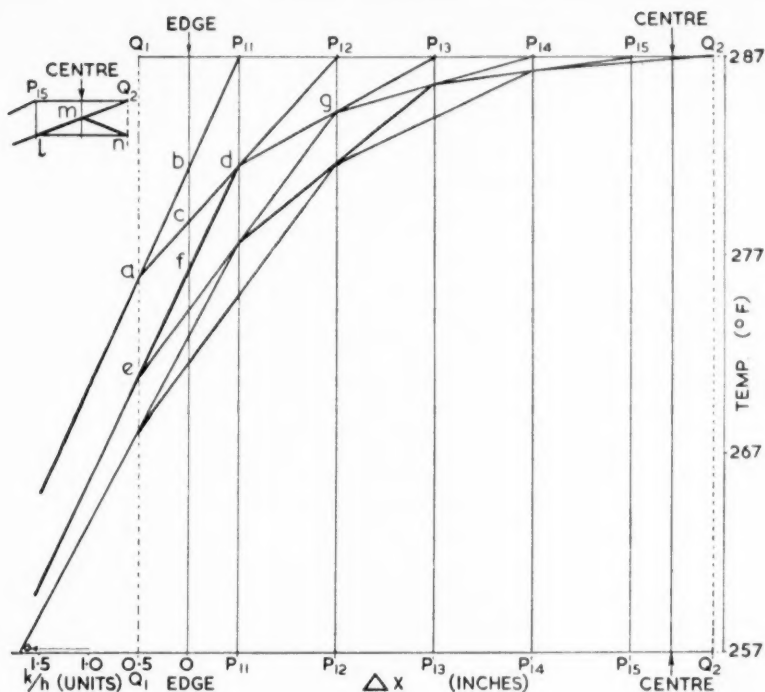


FIG. 1.

average temperature is assumed during the period. The intensity of vulcanization at a constant temperature multiplied by the time gives the amount of vulcanization during phase 2. The whole amount of vulcanization is obtained for the $\frac{1}{10}$ -inch sheet and for the thicker sheets at the standard time for the technical cure. The shortages are found and the extra vulcanization times readily ascertained.

The Schmidt method² was used to determine the progressive increases in temperature with time of the sheets of rubber during phase 1 and the progressive decreases during phase 3.

Quantitative results for the problem can be obtained only if the conditions are standardized. The following conditions and assumptions were adopted:

1. The unvulcanized mix is stored at room temperature.
2. The mix is placed in intimate contact with the hot mold, which is kept at the vulcanizing temperature.
3. The temperature of vulcanization is kept constant.
4. The mix receives all the heat through the faces of the molds and none through the ends.
5. The length and breadth of the sheet of rubber are large compared with its thickness.
6. The sheet is removed at the exact end of the heating phases.
7. The sheet is hung vertically until it has reached a temperature at which the amount of vulcanization is negligible.

Theory of the method.—The Schmidt diagram is used for the solution of practical problems of heat conduction in the unsteady state, and has been described fully elsewhere³; therefore a short description of the theory of Schmidt's method which is based on Fourier's law will suffice. Schmidt divides a sheet by planes, Δx apart, e.g., a $\frac{1}{16}$ -inch sheet is divided by 10 imaginary planes $\frac{1}{160}$ inch apart (see Figure 1).

Fourier's law for heat conduction:

$$\frac{\delta T}{\delta t} = \alpha \frac{\delta^2 T}{\delta x^2} \quad (1)$$

where the temperature varies with both time and distance, is treated as a partial differential equation.

When $\Delta_i T$ represents a small increment of temperature during a small change of time, Δt , x being kept constant, and when $\Delta_x T$ represents a corresponding increment of temperature for a change Δx at constant time:

$$\frac{\Delta_i T}{\Delta t} = \alpha \frac{\Delta_x^2 T}{(\Delta x)^2}$$

or

$$\frac{\Delta_i T}{\Delta_x^2 T} = \alpha \frac{\Delta t}{(\Delta x)^2} \quad (2)$$

If Δt and Δx are chosen so that the right-hand side of Equation (2) equals $\frac{1}{2}$, then the temperature at any point and at any time on the Schmidt diagram is the arithmetic mean of two temperatures at a distance Δx on either side at a time Δt previously; the required temperature can be determined from the graph by drawing a straight line between the two previous temperatures. Figure 1 shows how the temperature at any fixed plane was obtained at any time.

The resistance to the transfer of heat between the mold and the rubber is negligible during phases 1 and 2, because the rubber is in intimate contact with the mold. Under such conditions the Schmidt method is used for phase 1 and the temperature is calculated arithmetically.

During phase 3 the resistance to the flow of heat from the rubber to the air is not negligible, and the temperature of the surface of the sheet of rubber must be found graphically. A heat balance gives the thermal conditions at the surface of the sheet. The heat conducted to the surface is dissipated into the air.

As the slope of the line crossing at the surface is $\left(\frac{\delta T}{\delta x}\right)_{x=0}$

$$k \left(\frac{\delta T}{\delta x}\right)_{x=0} = h(T_s - T_a)$$

or

$$\left(\frac{\delta T}{\delta x}\right)_{x=0} = \frac{T_s - T_a}{k/h} \quad (3)$$

Equation (3) gives the slope of the temperature line at the surface and the position of the construction point 0 on the diagram.

To obtain numerical values for the heat transfer coefficients for a sheet in a vertical position, an expression⁴:

$$h = 0.275 \left(\frac{T_s - T_a}{L}\right)^{\frac{1}{4}} \quad (4)$$

which is true for sheets up to 3 feet high, was used. In the present paper the height of the sheet is assumed to be 10 inches, the same as that of the test sheet. The effect of radiation is small and is ignored.

The amount of vulcanization per period of time is the intensity of vulcanization at any temperature multiplied by the length of the period of time determined by the Schmidt diagram; it can be obtained at any plane in the rubber. The intensity of vulcanization has been taken as a function of temperature only, and has been assumed to be independent of time during the period of vulcanization. It has long been known that the rate of combination of rubber and sulfur at constant temperature does not vary until most of the sulfur has reacted, although accelerators modify this rate. Gordon⁵ has recently shown that the reaction is of the first order, at least initially. The course of the vulcanization is generally followed by a consideration of some physical property of a vulcanized mix, and the situation is further complicated because no physical property satisfactorily follows the reaction of rubber and sulfur. Because all conditions are kept similar for the vulcanization of all sheets which are considered in the examples which follow, it was assumed that the intensity of vulcanization was independent of time, in conformity with previous workers⁶ who had fixed unit intensity of vulcanization at 240° F, and had obtained the following expression to connect the intensity with temperature:

$$I = 2^{\frac{T-240}{15}} \quad (5)$$

Where 2 represents the temperature coefficient

$$= \frac{\text{rate of reaction at } T + 15^\circ \text{ F}}{\text{rate of reaction at } T^\circ \text{ F}}$$

This type of equation enables the intensity to be found at any temperature.

Example

To determine the extra time necessary to bring sheets $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ and 1 inch thick to the same degree of vulcanization as a sheet $\frac{1}{10}$ inch thick.

Data.—The mix is a tire-tread⁷ for which the best technical cure for a $\frac{1}{10}$ inch thick sheet is assumed to be 40 minutes with steam at 40 lb. per sq. in. gauge pressure (287° F).

Average thermal diffusivity⁷ = 0.0131 sq. in. per min. over the range 80–290° F. This includes the heat of vulcanization, which is small.

Temperature coefficient of vulcanization⁷ = 2.5 per 10° C or 18° F.

Room temperature = 67° F (assumed).

Calculations.—These are made according to the plan described above.

All calculations for the Schmidt diagrams for phase 3 require the thermal conductivity of the mix in British units. The thermal conductivity of a mix is an additive property⁸ of the volume-fractions of the components and is found as follows:

	Weight	Density	Volume	Volume fraction	$k \times 10^{-3}$	$\frac{k \times \text{vol. fraction}}{\times 10^{-3}}$
Hevea smoked sheet	100	0.92	108.7	0.786	32	25.1
Channel black	50	1.80	27.78	0.200	56	11.2
Zinc oxide	3	5.57	0.54	0.004	142	0.6
Sulfur	2.75	2.07	1.33	0.010	12	0.1
			138.35	1.000		37.0

Other components of the mix for which no values for thermal conductivity exist are: stearic acid 3, P.B.N. 1, M.B.T. 1.35. Thermal conductivity coefficient for the mix = 0.000037 cal. cm./sq. cm. sec. ° C, or 0.0895 B.T.U. ft./sq. ft. hr. ° F.

Part of a Schmidt diagram for phase 3 for a $\frac{1}{2}$ -inch thick sheet is given in Figure 1 (p. 4) and illustrates the construction of the diagram. Δx is taken as abscissa. A fairly large scale for temperature as ordinate is taken to ensure clarity when drawing lines for temperatures below 200° F. Other sheets follow a similar pattern for phase 3.

Heat is lost by the sheet on both sides, therefore it is necessary to consider and draw only half the thickness.

Let the sheet be divided into layers each $\frac{1}{20}$ inch thick for Δx .

From the modified Equation (2):

$$\begin{aligned}\alpha \frac{\Delta t}{(\Delta x)^2} &= \frac{1}{2} \\ \Delta t &= \frac{1}{2} \cdot (\Delta x)^2 \cdot \frac{1}{\alpha} \\ &= \frac{1}{2} \cdot \left(\frac{1}{20}\right)^2 \cdot \frac{1}{0.0131} \cdot 60 \text{ sec.} \\ &= 5.72 \text{ sec.}\end{aligned}$$

which is the time of one period.

It is found throughout this work that k/h which has the dimensions of length is greater than $\Delta x/2$; therefore it is necessary³ to draw a construction line Q_1 on the left-hand side of the line representing the surface or edge of the sheet and at a distance $\Delta x/2$ from it.

The first plane P_{11} is drawn on the right-hand side of the line representing the edge and at a distance $\Delta x/2$ from it. Lines for planes, P_{12} , P_{13} , P_{14} , P_{15} , distances Δx apart, representing $\frac{1}{20}$ inch, are drawn. The center line of the sheet is drawn on the right-hand side of plane P_{15} at a distance $\Delta x/2$ from it and another construction line Q_2 is drawn at a distance Δx on the right-hand side of plane P_{15} .

The first line on the diagram joins the construction point 0 to the point P_{11} . 287° F; 0 is always fixed on the ordinate T_a (67° F), its position on T_a on the left of the plane edge is variable and is found from the value of k/h . The first position of 0 is found as follows:

$$\begin{aligned}T_s - T_a &= 287 - 67^\circ \text{ F} = 220^\circ \text{ F} \\ k &= 0.0895 \text{ B.T.U. ft./sq. ft. hr. } ^\circ \text{ F} \\ h &= 0.275 \left(\frac{T_s - T_a}{L} \right)^{\frac{1}{4}} \\ &= 0.275 \left(\frac{220}{10/12} \right)^{\frac{1}{4}} \\ &= 1.11 \text{ B.T.U./sq. ft. hr. } ^\circ \text{ F} \\ k/h &= \frac{0.0895}{1.11} = 0.0806 \text{ ft.} = 0.967 \text{ in.}\end{aligned}$$

The distance between the planes is $\frac{1}{20}$ inch, which is a unit distance on Figure 1; therefore 0.967 inch or $0.967 \times 20 = 19.34$ units on the left of EDGE

TABLE I
TEMPERATURES ($^{\circ}$ F) AND AMOUNTS OF VULCANIZATION (V) AT VARIOUS PLANES
 $\frac{1}{2}$ INCH SHEET—PHASE 3

Period	Construction point		Edge		P_{11}		P_{12}		P_{13}		P_{14}		P_{15}		Center	
	$^{\circ}$ F	Length	$^{\circ}$ F	V	$^{\circ}$ F	V	$^{\circ}$ F	V	$^{\circ}$ F	V	$^{\circ}$ F	V	$^{\circ}$ F	V	$^{\circ}$ F	V
1	265	1.484	281 $\frac{1}{2}$	0.779	287	1.044	287	2.087	287	3.131	287	4.175	287	5.219	287	5.219
2	—	—	279 $\frac{1}{2}$	0.721	281 $\frac{1}{2}$	1.558	287	2.087	287	3.131	287	4.175	287	5.219	287	5.219
3	260	1.505	276	0.596	281 $\frac{1}{2}$	1.558	284 $\frac{1}{2}$	1.815	284 $\frac{1}{2}$	1.934	287	4.175	287	5.219	287	5.219
4	—	—	274 $\frac{1}{2}$	0.545	277 $\frac{1}{2}$	1.287	284 $\frac{1}{2}$	1.815	285 $\frac{1}{2}$	1.934	287	4.175	287	5.219	287	5.219
5	257	1.522	272 $\frac{1}{2}$	0.499	277 $\frac{1}{2}$	1.287	281 $\frac{1}{2}$	1.578	285 $\frac{1}{2}$	1.934	286 $\frac{1}{2}$	2.009	287	5.219	287	5.219
6	—	—	270 $\frac{1}{2}$	0.456	274 $\frac{1}{2}$	0.545	281 $\frac{1}{2}$	1.578	284	0.896	284 $\frac{1}{2}$	2.009	286 $\frac{1}{2}$	1.031	286 $\frac{1}{2}$	1.031

TABLE II
TEMPERATURES AND AMOUNTS OF VULCANIZATION (V) AT VARIOUS PLANES
1 $\frac{1}{16}$ INCH SHEET—PHASE I

Amount of vulcanization at the edge or surface = 5.720 units

Time (sec.)	Periods	P_1			P_2			P_3			P_4			Center		
		Temp. (° F)	V (units)	V (units)	Temp. (° F)	V (units)	V (units)	Temp. (° F)	V (units)	V (units)	Temp. (° F)	V (units)	V (units)	Temp. (° F)	V (units)	V (units)
5	1-22	257 $\frac{1}{2}$	0.089	0.016	228 $\frac{1}{2}$	0.016	0.004	210 $\frac{1}{2}$	0.004	0.004	192 $\frac{1}{2}$	0.002	0.002	192 $\frac{1}{2}$	0.002	0.002
10	23-44	277 $\frac{1}{2}$	0.404	0.203	269 $\frac{1}{2}$	0.203	0.122	261 $\frac{1}{2}$	0.122	0.122	258 $\frac{1}{2}$	0.089	0.089	255 $\frac{1}{2}$	0.080	0.080
15	45-66	283 $\frac{1}{2}$	0.693	0.543	281 $\frac{1}{2}$	0.543	0.448	278 $\frac{1}{2}$	0.448	0.448	277 $\frac{1}{2}$	0.397	0.397	276 $\frac{1}{2}$	0.381	0.381
20	67-87	285 $\frac{1}{2}$	0.794	0.729	284 $\frac{1}{2}$	0.729	0.682	284 $\frac{3}{4}$	0.682	0.682	283 $\frac{3}{4}$	0.653	0.653	282 $\frac{3}{4}$	0.644	0.644
25	88-109	286 $\frac{1}{2}$	0.887	0.862	286 $\frac{1}{2}$	0.862	0.842	286 $\frac{1}{2}$	0.842	0.842	285 $\frac{1}{2}$	0.830	0.830	285 $\frac{1}{2}$	0.862	0.862
30	110-131	286 $\frac{1}{2}$	0.906	0.899	286 $\frac{1}{2}$	0.899	0.890	286 $\frac{1}{2}$	0.890	0.890	286 $\frac{1}{2}$	0.886	0.886	286 $\frac{1}{2}$	0.886	0.886
31	132-137	286 $\frac{1}{2}$	0.250	0.247	286 $\frac{1}{2}$	0.247	0.247	286 $\frac{1}{2}$	0.247	0.247	286 $\frac{1}{2}$	0.245	0.245	286 $\frac{1}{2}$	0.244	0.244
			4.023	3.499		3.499	3.235		3.235			3.102			3.063	

Vulcanization at edge = 35.75 units

Vulcanization at edge = 35.75 units (min.)	Periods	P_1			P_2			P_3			P_4			Center		
		Temp. (° F)	V (units)	V (units)	Temp. (° F)	V (units)	V (units)	Temp. (° F)	V (units)	V (units)	Temp. (° F)	V (units)	V (units)	Temp. (° F)	V (units)	V (units)
1	1-42	276 $\frac{1}{2}$	2.715	1.168	267 $\frac{1}{2}$	1.168	0.646	259	0.646	0.646	255 $\frac{1}{2}$	0.454	0.454	252 $\frac{1}{2}$	0.401	0.401
2	43-84	285 $\frac{1}{2}$	8.874	7.453	284 $\frac{1}{2}$	7.453	6.534	283 $\frac{3}{4}$	6.534	6.534	283 $\frac{3}{4}$	5.976	5.976	282 $\frac{3}{4}$	5.863	5.863
3	85-126	286 $\frac{1}{2}$	10.658	10.416	286 $\frac{1}{2}$	10.416	10.222	286 $\frac{1}{2}$	10.222	10.222	286 $\frac{1}{2}$	10.105	10.105	286 $\frac{1}{2}$	10.066	10.066
34	127-137	286 $\frac{1}{2}$	2.850	2.834	286 $\frac{1}{2}$	2.834	2.821	286 $\frac{1}{2}$	2.821	2.821	286 $\frac{1}{2}$	2.805	2.805	286 $\frac{1}{2}$	2.801	2.801
			25.097	21.871		21.871	20.223		20.223			19.340			19.131	

Vulcanization at edge = 142.98 units		1-inch sheet—phase 1				
2	1-21	257 $\frac{1}{2}$	1.995	228 $\frac{1}{2}$	0.340	210 $\frac{1}{2}$
4	22-42	276 $\frac{1}{2}$	9.066	267 $\frac{1}{2}$	4.335	259
6	43-63	283 $\frac{1}{2}$	15.949	279 $\frac{1}{2}$	12.006	277 $\frac{1}{2}$
8	64-84	285 $\frac{1}{2}$	19.547	284 $\frac{1}{2}$	17.720	283 $\frac{1}{2}$
10	85-105	286 $\frac{1}{2}$	21.057	286 $\frac{1}{2}$	20.309	285 $\frac{1}{2}$
12	106-126	286 $\frac{1}{2}$	21.574	286 $\frac{1}{2}$	21.325	286 $\frac{1}{2}$
13	127-137	285 $\frac{1}{2}$	11.502	286 $\frac{1}{2}$	11.336	286 $\frac{1}{2}$
			110.690		87.461	
					0.090	192 $\frac{1}{2}$
					2.494	255 $\frac{1}{2}$
					9.874	275 $\frac{1}{2}$
					16.362	283 $\frac{1}{2}$
					19.791	285 $\frac{1}{2}$
					21.095	286 $\frac{1}{2}$
					11.283	286 $\frac{1}{2}$
					80.989	
					77.557	
					0.038	192 $\frac{1}{2}$
					1.777	252 $\frac{1}{2}$
					8.512	275 $\frac{1}{2}$
					15.590	282 $\frac{1}{2}$
					19.440	283 $\frac{1}{2}$
					20.982	285 $\frac{1}{2}$
					11.218	286 $\frac{1}{2}$
						11.204
						0.029
						1.568
						8.143
						15.309
						19.335
						20.931
						11.204
						76.519

Vulcanization at edge = 321.71 units		1-inch sheet—phase 1				
10	1-46	278 $\frac{1}{2}$	30.63	271 $\frac{1}{2}$	14.35	264 $\frac{1}{2}$
20	47-93	286 $\frac{1}{2}$	94.05	285 $\frac{1}{2}$	82.37	284 $\frac{1}{2}$
29 $\frac{1}{2}$	94-137	286 $\frac{1}{2}$	101.52	286 $\frac{1}{2}$	100.05	286 $\frac{1}{2}$
			226.20		196.77	
					9.57	261 $\frac{1}{2}$
					74.61	284 $\frac{1}{2}$
					96.83	286 $\frac{1}{2}$
					181.01	
					6.32	258 $\frac{1}{2}$
					70.07	284 $\frac{1}{2}$
					96.12	286 $\frac{1}{2}$
					172.51	
					5.68	258 $\frac{1}{2}$
					68.64	284 $\frac{1}{2}$
					95.87	286 $\frac{1}{2}$
					170.19	

Vulcanization at edge (52 $\frac{1}{2}$ minutes) 572.32 units		1-inch sheet—phase 1				
20	1-52 $\frac{1}{2}$	280 $\frac{1}{2}$	72.01	275 $\frac{1}{2}$	38.04	270 $\frac{1}{2}$
40	53-105 $\frac{1}{2}$	286 $\frac{1}{2}$	198.48	286 $\frac{1}{2}$	181.22	285 $\frac{1}{2}$
52 $\frac{1}{2}$	106-137 $\frac{1}{2}$	286 $\frac{1}{2}$	131.92	286 $\frac{1}{2}$	130.67	286 $\frac{1}{2}$
			402.41		349.93	
					24.86	268 $\frac{1}{2}$
					169.20	285 $\frac{1}{2}$
					129.53	286 $\frac{1}{2}$
					323.59	
					19.36	266 $\frac{1}{2}$
					162.09	285 $\frac{1}{2}$
					128.81	286 $\frac{1}{2}$
					310.26	
					17.78	266 $\frac{1}{2}$
					159.81	285 $\frac{1}{2}$
					128.56	286 $\frac{1}{2}$
					306.15	

$\frac{3}{4}$ -inch sheet—phase 3

10	1-46	220	15.63	225	21.33	234	31.92	240	42.04	245	50.59	247	56.29	248	57.28
20	47-93	188	1.75	192	2.20	198	3.21	203	4.35	206	5.39	209	6.17	209	6.31
30	94-139	164	0.40	167	0.57	171	0.63	176	0.78	178	0.92	180	1.02	180	1.04
40	140-186	145	0.13	147	0.15	151	0.19	154	0.23	156	0.26	157	0.28	158	0.28
50	187-209	138	0.03	140	0.04	143	0.04	146	0.05	147	0.06	149	0.06	149	0.06
			17.94		24.29	(30.23)	35.99	(41.76)	47.45	(52.79)	57.22	(61.98)	63.82		64.97

1-inch sheet—phase 3

20	1-52	201	18.25	206	28.74	216	46.64	223	65.58	229	80.29	232	90.97	233	92.91
40	53-105	164	1.15	168	1.49	173	2.25	179	3.14	182	4.02	185	4.67	185	4.79
60	106-157	138	0.22	141	0.26	145	0.34	149	0.43	151	0.50	153	0.55	153	0.56
80	158-209	120	0.07	122	0.08	125	0.10	128	0.11	129	0.13	131	0.14	131	0.14
90	210-235	113	0.02	115	0.02	117	0.02	120	0.03	121	0.03	122	0.03	122	0.03
			19.71		30.59	(39.98)	49.35	(59.45)	69.30	(77.58)	84.97	(91.34)	96.36		98.43

at 67° F is the position of 0. This point should be joined to P_{11} .287° F, and the line is awkward to draw when a large scale is used for the temperature; therefore the principle of similar triangles is used at a $\frac{1}{10}$ th scale. By this principle the ordinate for temperature is:

$$287 - \frac{287 - 67}{10} = 265^\circ \text{ F}$$

The abscissa for k/h is:

$$\frac{19.34 + 0.5}{10} - 0.5 = 1.484$$

because the height of the large triangle is situated at the plane P_{11} , but the distance k/h is measured from the plane EDGE. The first line is drawn from the point 1.484 units from EDGE/265° F to P_{11} .287° F, cutting Q_1 and EDGE at a and b , respectively, where b represents the temperature of the edge of the sheet at period 1. The next line joins a and P_{12} .287° F, giving temperatures of the edge and plane P_{11} for period 2 at the points c and d . The new edge temperature, c , is used to calculate h for the new position of the construction point 0; the temperature d is used to fix the new ordinate for temperature by the principle of similar triangles as before. The new coordinates representing 0 are joined to d , and d is joined to P_{13} .287° F, these lines cut Q_1 at e and also obtain temperatures f , d and f for period 3. All temperatures and construction lines are tabulated in Table I. Temperatures for period 5 are obtained by joining e and g , g and P_{14} .287° F. Alternate, equidistant planes are joined, and construction points 0 are calculated until a line from P_{14} joins Q_2 to give temperatures, l , m , and 287° F for planes P_{15} , CENTER, and Q_2 respectively. Although Q_2 is a construction line, it represents a plane in the sheet at a distance from the center similar to that of plane P_{15} and is at a similar temperature. Thus l and m represent the temperatures of planes P_{15} and CENTER for period 6, but the temperature of Q_2 is corrected when, in the next period, the line joining the temperature of plane P_{13} to l is drawn, then l and the plane Q_2 are joined by a line l , n , parallel to the Δx axis and m and n are joined. This construction is shown enlarged but not to scale at the left-hand top of Figure 1. Temperatures at the ends of various periods for this and for the other sheets are shown in Table II, and they are obtained by a continuation of the routine outlined above.

Temperatures at the edge of the sheet and at the plane P_{11} were taken from the Schmidt diagram, but the temperatures of the other planes are arithmetical averages, calculated to the nearest $\frac{1}{4}$ ° F. However, the diagram must be drawn because the lines are interdependent. When the average is an inexact $\frac{1}{4}$ ° F, a temperature greater than the true average alternates with one less.

The Schmidt diagram and method for phase I are simple, and the temperatures may be obtained arithmetically throughout, but until sufficient practice in the arithmetical method has been gained, it is better to draw the diagram as a check on the arithmetic. The temperature scale on the diagram (Figure 1) is reversed to show 67° F at the top of the diagram. Six equidistant planes Δx apart are drawn, i.e., edge, P_1 , P_2 , P_3 , P_4 and center, and the change in the positions should be noted. Close contact causes zero resistance between the mold and the cold sheet; therefore it is assumed that the edge of the sheet assumes a temperature of 287° F at once. At period 1 the plane P_1 has a calculated temperature midway between that of the edge and plane P_2 :

$$\frac{287 + 67}{2} = 177^\circ \text{ F}$$

The temperature of the center plane is made equal to that of P_4 during every alternate period. By calculating averages, as for temperatures of the mid-planes of Table I, the temperatures are tabulated and are given an accuracy of $\frac{1}{16}^\circ\text{F}$, because the temperatures increase slowly as the constant vulcanizing temperature is approached.

To avoid recording large numbers of figures, the temperatures at the ends of suitable periods are stated in Table II, where, in addition, the amounts of vulcanization to the end of the last period are given.

The intensity of vulcanization is calculated from an adaptation of Equation (5); a temperature coefficient of 2.5 per 18°F is used; therefore Equation (5) becomes:

$$I = 2.5^{\frac{T-240}{18}}$$

or

$$\log_{10} I = 0.39794 \cdot \frac{T - 240}{18}$$

The amount of vulcanization during two periods at constant temperature is obtained by multiplying the intensity at that temperature by the length of a double period in minutes. A variation of this calculation is shown for the amount of vulcanization at the edge of a $\frac{1}{16}$ -inch thick sheet as follows:

Temperature of edge = 287°F

$$\begin{aligned}\log_{10} I &= 0.39794 \cdot \frac{287 - 240}{18} \\ &= 0.022108 \times 47 = 1.03906 \\ I &= 10.94 \text{ units/min.}\end{aligned}$$

Amount of vulcanization during 2 periods of

$$\begin{aligned}0.22896 \text{ sec. each} &= \frac{0.22896}{60} \cdot 2 \cdot I \\ &= 0.007632 \cdot I\end{aligned}$$

Amount of vulcanization at the edge during 137 periods

$$\begin{aligned}&= 0.007632 \times \frac{137}{2} \times 10.94 \\ &= 5.720 \text{ units}\end{aligned}$$

The number of calculations of the amount of vulcanization was reduced by calculating the intensity for intervals of $\frac{1}{4}^\circ\text{F}$, *e.g.*, the intensity at 285°F was taken as equal to the intensities for all temperatures between $284\frac{1}{4}$ and $285\frac{1}{4}^\circ\text{F}$.

Other temperatures were grouped appropriately as $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}^\circ\text{F}$.

The times in Table II approximately correspond to the end of the last period stated in column 2. The figures in brackets between the total amounts of vulcanization for planes P_{11} , P_{12} , etc., in phase 3 are the total amounts of vulcanization at planes P_1 , P_2 , etc., and they are used in Table III to determine the amounts of vulcanization at equidistant planes in the sheets. They are obtained from a graph of the vulcanization of planes P_{11} to P_{15} .

The amounts of vulcanization shown in Table II are summarized in the first six *V* columns of Table III, and the amounts obtained during phase 2 are added. The average vulcanization of the planes P_3 , P_4 and center of the $\frac{1}{10}$ -inch sheet is the desired amount of vulcanization for all the center parts of the sheets. Column 9 shows the average vulcanization of these planes for all sheets. The 1-inch sheet is a special case because its center has not reached the constant vulcanizing temperature in 40 minutes, but the 52½ minute results are recorded and the extra 12½ minutes are added to the calculated extra time. The shortage of the amounts of vulcanization are recorded in column 10, and, when these are divided by the intensity at 287° F, the extra time is recorded in column 11. Column 12 shows the amounts of vulcanization on a percentage basis, the extra time being added to phase 2.

DISCUSSION OF RESULTS

The division of the vulcanization process into three phases and the calculation of the amounts of vulcanization according to the temperature has enabled a calculation of the vulcanization time to be made for various thicknesses of soft rubber under certain standard conditions.

The technique of calculating the temperatures for phase 1 by the Schmidt method is easily mastered, and the amounts of vulcanization obtained in phase 1 for all sheets greater than $\frac{1}{10}$ inch thick is greater than in phase 3; for the thickest sheets it is much greater. The accuracy of calculations for phase 3 is less than for phase 1; the thermal conductivity for some common constituents of nearly all mixes is unknown, it has no temperature coefficient, and the system by which it is calculated precludes easy computation of such a coefficient; the heat-transfer coefficient has been calculated to a second decimal place, which is by no means certain. The temperatures of the edge and the first plane during phase 3 are obtained by a graphical method; this is another disadvantage. For these reasons the temperature was calculated to the nearest $\frac{1}{4}$ ° F throughout phase 3, and even with such temperature intervals, the Schmidt diagrams for the $\frac{1}{10}$ - and $\frac{1}{4}$ -inch sheets could not be completed because the temperature interval between periods for the edge disappeared after the times shown in Table II, and it is probable that one unit should be added to the desired vulcanization obtained for the $\frac{1}{10}$ -inch sheet. The amount of vulcanization in phases 1 and 3 is small below 160° F.

It has long been known that overvulcanization takes place at the surface of sheets of soft rubber. The overvulcanization at the surface of a $\frac{1}{10}$ -inch sheet, as shown in Table III, is very small, but it increases for thicker sheets until it is quite large for the $\frac{3}{4}$ - and 1-inch sheets. Except for the $\frac{3}{4}$ - and 1-inch sheets, this overvulcanization does not extend very far beyond plane 1. The uniformity of vulcanization of planes P_2 to the center in any one sheet is good, and for this reason it was decided to calculate the extra time needed for a full technical cure on the average vulcanization of planes P_3 , P_4 , and CENTER.

Figure 2 shows the rapidity of the increase of the extra time for the thicker sheets. When the extra time is calculated with greater accuracy than is shown in Table III, the extra time is almost, but not quite, directly proportional to the square of the thickness. A plot of extra time *vs.* thickness will provide a graph from which the extra time can be obtained for any thickness up to 1 inch. Any accuracy greater than one minute is not considered of interest to rubber technologists.

The last column of Table III shows the phase vulcanization at the center of the sheet expressed as percentage of the desired vulcanization. These results may be applied to other examples when it is assumed that the percentage vulcanization obtained during phases 1 and 3 is a function of the thickness of the sheet. The time, temperature and vulcanization intensity are found for the $\frac{1}{10}$ -inch sheet, and the amount of vulcanization is calculated. Phase 1 vulcanization for the sheet of the desired thickness is calculated by the method shown.

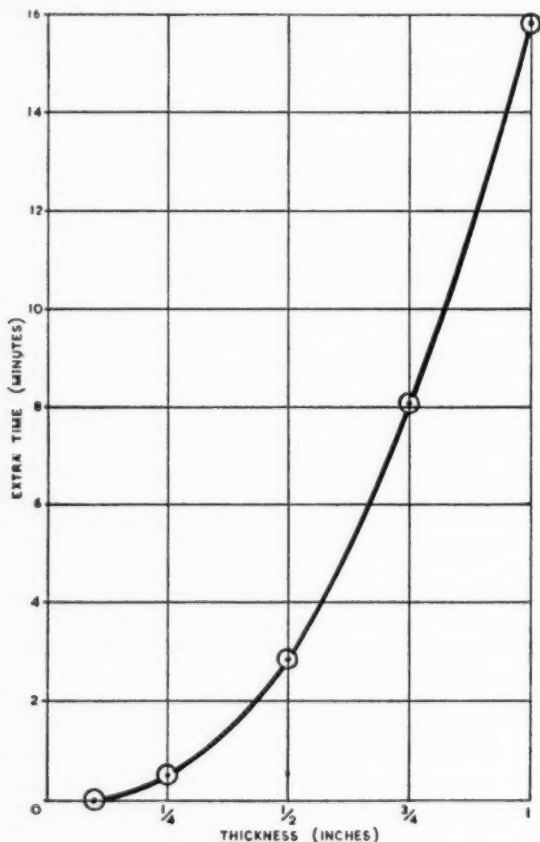


FIG. 2.

The percentage vulcanization for phases 1 and 3 from the last column of Table III are plotted against the thickness; curves which are similar in shape to the curve on Figure 3 are obtained. Phase vulcanizations are taken from the curve and used to calculate phase 3 vulcanization. Phase 2 vulcanization and the shortage are ascertained and the extra time is easily calculated. The procedure is illustrated better by an example than by a description, and this is done below, where arbitrary units and times are used.

Example

To determine the time required for a full technical vulcanization of a $\frac{9}{16}$ -inch thick sheet of a mix.

Data.—The best vulcanization for a $\frac{1}{16}$ -inch sheet is 50 minutes at a vulcanization intensity of 10.1 units per minute.

Calculations.—The desired vulcanization is $10.1 \times 50 = 505$ units.

Phase 1 vulcanization for the central planes of the $\frac{9}{16}$ -inch sheet is 130 units in 32 minutes.

Phase 2 vulcanization = $10.1 \times 18 = 182$ units.

From the graphs of phases 1 and 3, phase 1 vulcanization is 21.3 per cent, and phase 3 vulcanization is 9.8 per cent for the thick sheet.

∴ Phase 3 vulcanization = $130 \times \frac{9.8}{21.3} = 60$ units.

Total vulcanization in 50 minutes = $130 + 182 + 60 = 372$ units.

Shortage of vulcanization = $505 - 372 = 133$ units.

Extra time needed = $133/10.1 = 13$ minutes.

The calculation of the desired vulcanization by the above method introduces little error; inspection of Table III shows it to be 0.16 per cent low for the example shown.

It is realized that the theory and the worked example makes use of methods which are not usual in the rubber industry, but the method should prove useful to the technologist when the properties of the rubbers have been obtained. The method is limited to flat sheets of soft rubbers.

It is also realized that the use of an average value for the thermal diffusivity and additive values for the thermal conductivity introduce errors in the calculations. The use of accurate correlations of these properties with temperature would improve the accuracy of the method at the cost of further complication of the calculation.

SUMMARY

Schmidt's method for the determination of temperatures attained by various thicknesses of solid sheets during heating and cooling is adapted for the calculation of the amounts of vulcanization obtained for flat sheets of soft rubber and of the extra time needed to obtain a full vulcanization in the center of the sheets. The uniformity of vulcanization of the central portion of the sheets is investigated.

NOMENCLATURE

All properties relate to the rubber mix except where otherwise stated.

α = coefficient of thermal diffusivity = $\frac{k}{\rho}$ (sq. in. per min.).

k = coefficient of thermal conductivity (B.T.U. ft. per sq. ft. hr. ° F.).

s = specific heat.

ρ = density (lb. per cu. ft.).

T = temperature (° F.).

t = time (seconds).

x = distance from one face of the sheet (ft.).

h = coefficient of heat transmission (B.T.U. per sq. ft. hr. ° F.).

L = height of sheet (ft.).

I = intensity of vulcanization (units per min.).

V = amount of vulcanization (units).

Suffixes

_s = surface or edge.

_a = air.

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STUDIES ON THE YELLOW FRACTION OF LATEX *

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The investigations described in this paper are part of the studies of fresh latex carried out at the INIRO (Indonesian Rubber Research Institute). For readers not acquainted with the special subject, it may be useful to mention that Homans and van Gils¹ have found that fresh Hevea latex is not solely a dispersion of rubber globules in an aqueous medium, the serum, but that there are also present large colloidal jellylike units or agglomerations of them, constituting a separate phase in the rubber dispersion. These bodies were called lutoids by the discoverers, because they contained the yellow coloring substances of the rubber. Under a microscope, however, these lutoids look like transparent islands against a darker background of rubber particles.

After centrifugation, the lutoids are separated at the bottom of the tube and look like a viscous yellowish jellylike mass, containing a low percentage of rubber. It is also possible to separate this mass by other means. As a whole, these agglomerations of lutoids are called the yellow fraction. The remaining latex is called the white fraction.

Investigations carried out at the Rubber Research Institutes in Indonesia and Malaya have shown that the lutoids are responsible for many phenomena occurring in fresh latex. Recent studies of Ruinen² seem to indicate that the lutoids are also involved in the rubber formation in the tree.

DISSOLUTION OF THE LUTOIDS

According to the previous investigation mentioned, the lutoids dissolve completely on addition of ammonia to latex. They become invisible under the microscope and can no longer be separated by centrifugation in tubes.

However, it has now been established that this dissolution is only partial and that an undissolved part is dispersed into small round globules of semisolid consistency. On careful examination in a microscope with high magnification, the author saw that the rubber globules were not regularly distributed throughout the space, but that there were small empty spots between them. Brownian movement of the particles interfered with these observations.

In very thin layers, however, these empty spots are easier to observe, and then they look like round globules or droplets, 3 to 10 μ in diameter. Pressing down the coverglass by means of a clamp causes these globules to increase in size.

These phenomena are not discernible in centrifuged latex. These round globules can be separated by centrifuging with a highspeed De Laval or Sharples centrifuge. They are found on the walls of the centrifuge bowl as a butter-like mass³.

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Owing to the small size, separation is possible only by high-speed centrifugation. The existence of lutoid remnants in ammoniated latex has also been mentioned by Ruinen⁴.

Another indication of the existence of undissolved lutoids in ammoniated latex is the following.

Homans has made a large number of viscosity determinations of ammoniated field latex and of the white fraction prepared from this latex. By calculating the voluminosity ($= V_R$) from these figures it was found that the V_R of ordinary ammoniated latex is much higher than the V_R of ammoniated white fraction latex⁵. The voluminosity is defined as the ratio between the rheologically active volume of the dispersed phase and the volume, determined by analytical means.

In other words, besides the rubber phase there must be another phase present which contributes to the viscosity of ammoniated latex as well. The importance of this fact for processes involved in the concentration of latex is only indicated here.

ADDITION OF WATER

In contrast to the addition of ammonia, the addition of water stiffens and immobilizes the lutoids.

If latex is diluted with water, one expects the viscosity to be lowered owing to the decrease of the D.R.C. (dry rubber content). However, the first effect observed is an increase of the viscosity as can be seen from the following experiment:

Water added to 50 cc. latex (cc.)	Viscosity at 30° C (centipoises)
0	21.2
0.5	21.7
1	22.8
2	23.0
4	25.2
8	30.7
15	Not measurable with capillary viscom- eter

Latex: D.R.C. = 36.8%; T.S. (total solids) = 39.5%

In connection with the mentioned phenomenon, the author observed that, after dilution, separation of the yellow fraction by centrifugation was nearly impossible. When the dilution is accompanied by mechanical treatment, stirring, or, even better, rolling in a ball mill, the lutoids are forced to cohere, thus forming agglomerates and even clots. After some time the whole yellow fraction can be separated as one coherent coagulum.

When a current of air is passed through the latex, the lutoids move upward with the air bubbles and separate in the foam.

DISSOLUTION OF THE LUTOIDS BY SALTS

Originally it was believed that the lutoids would remain the same if the latex was not diluted with water but with a solution of about the same ionic strength as the latex itself.

Indeed, it is possible to make the dilution—for instance, with a 0.1 *N* potassium chloride solution—and still obtain a separation of the yellow fraction after

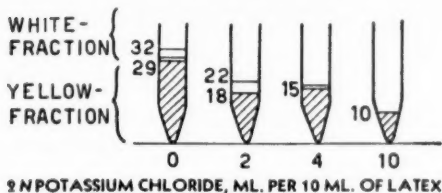


FIG. 1.—Reduction of volume of the yellow fraction by addition of salts.

centrifuging. However, if a certain amount of yellow fraction is redispersed in a salt solution and again centrifuged, a smaller volume is obtained. By repeating the procedure, the volume obtained after each separation decreases. Different salts in varying concentrations and also a combination of primary and secondary phosphates of the same pH as the original latex have been tried in the author's laboratory but there was no success in obtaining a yellow fraction "washed out" and in equilibrium with the salt solution.

It appears that neutral salts dissolve certain parts of the yellow fraction, the amount dissolved depending on the strength of the salt solution. This will be made clear by Figures 1 and 3 which show the volume of the yellow fraction reduced by increasing amounts of sodium, lithium, ammonium, and potassium chlorides; sodium sulfate; sodium nitrate; and sodium phosphate.

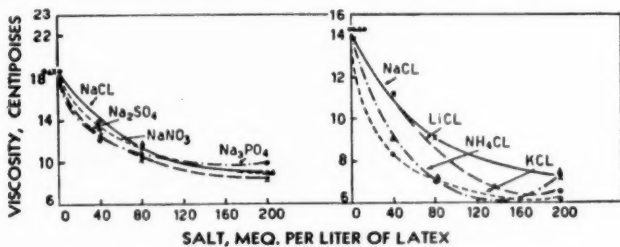


FIG. 2.—Influence of salts on the viscosity of latex.

Salts with divalent cations have a coagulating effect on the yellow fraction and are, therefore, not taken into consideration.

The following phenomena are also remarkable.

1. The yellow coloring substances of the latex do not dissolve, but remain in the yellow fraction. Sometimes these substances separate in a ring a little below the boundary of the yellow fraction (see Figure 1).

2. The addition of salts also reduces the viscosity of the latex considerably. Even lower viscosities are attainable in this way than by addition of ammonia (Figure 4).

DISCUSSION

By examining the curves in Figures 2 and 3, the author has tried to find some regularity, as, for instance, the influence of the lyotropic series, but he has not succeeded. However, this dissolution by neutral salts is not an uncommon phenomenon in colloid chemistry. By the interaction under proper conditions of hydrophylic colloids of opposite electric charge, so-called complex coacervates

may be formed⁸. Under the microscope these complex coacervates are very similar in appearance to lutoids.

Moreover, on addition of neutral salts, the coacervates are dissolved, owing to removal of the electric charge of the colloids.

It seems reasonable to assume, therefore, that the lutoids consist partly of so-called tricomplex coacervates, constituted out of negatively charged protein and lipid, and positively charged magnesium ions.

Quantitative considerations have shown that the drop in viscosity cannot be accounted for by the reduction of the volume of the yellow fraction. The

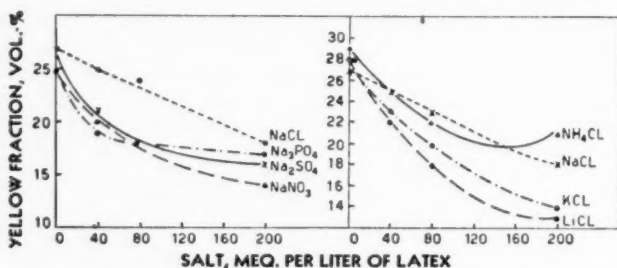


Fig. 3.—Influence of salts on the yellow fraction volume.

answer to this problem of reduced viscosity is found by investigating the white fraction. In Figure 5 it is seen that if salt is added to the white fraction of latex, the viscosity is decreased in the same way as with ammonia.

Therefore, in the author's opinion, the coacervate which dissolves in alkali as well as in salt solutions not only constitutes a part of the yellow fraction, but every rubber particle is enveloped with a coating of these coacervates, causing the rubber particles to agglomerate and hinder their Brownian movement, as may be observed by microscopic examination. Through the addition of alkali or salts the rubber particles are decoated and entirely free to move.

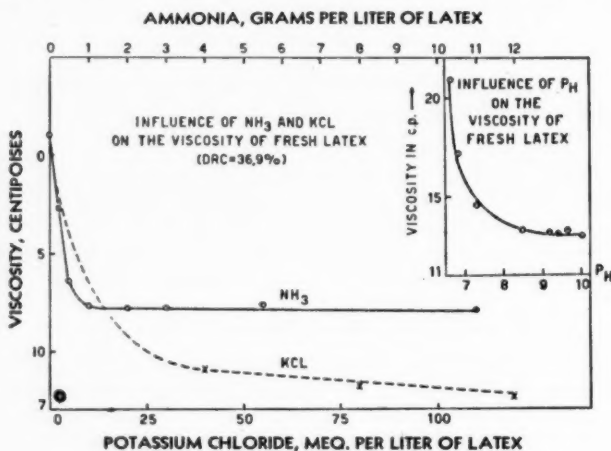


Fig. 4.—Influence of various factors on the viscosity of fresh latex.

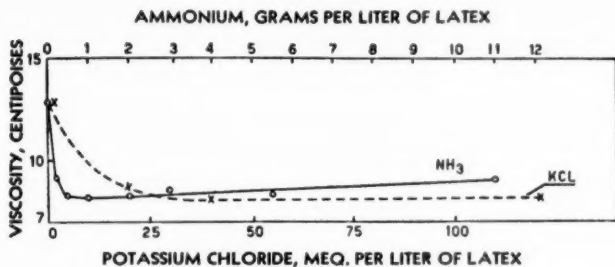


Fig. 5.—Influence of ammonia and potassium chloride on the viscosity of the white fraction of latex (DRC = 44.0%).

TECHNOLOGICAL ASPECTS

In ordinary estate practice, latex is coagulated after dilution with formic acid. Usually 4 grams of formic acid per kilogram of rubber is needed.

It is known that by addition of only a quarter of this amount and subsequent stirring the so-called yellow precoagulum is formed, which is composed of the yellow fraction plus a certain amount of adhering white fraction rubber. The rubber obtained after discarding the precoagulum is very white and can be worked up to sole crepe. The precoagulum gives rubber of inferior quality. However, if the precoagulation could proceed in such a way that the amount of precoagulum is as low as possible, this would be an advantage. The author has shown that this effect is obtainable through addition of salt to the latex before diluting and acidifying. As the yellow coloring substances are not dissolved, the precoagulum contains the total amount of the coloring substances that has to be discarded.

A second mode of operation is the following: it is not necessary to discard the yellow fraction by partial acid coagulation. If the latex can be kept liquid for at least 20 hours, the heavier lutoids will settle down to a more or less coherent layer at the bottom of the vessel if a sufficiently low viscosity is provided. The author has been successful in obtaining the result indicated by purposely adding salts and 0.1 per cent formaldehyde to the latex.

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CHARACTERIZATION OF CORD FATIGUE IN TIRES *

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Fatigue failure of tire cord has been studied for many years because it has an important influence on tire design and determines the suitability of materials for use in tire manufacture. Most previous work in the study of tire cord fatigue has centered in the development of empirical laboratory tests of cord fatigue or in an analysis of cords run on laboratory testers¹ rather than in the study of cords removed from fatigued tires. These studies have shown that cords run on laboratory testers do not undergo any significant changes in physical properties with running, other than a lowered breaking elongation.

The laboratory fatigue testers currently in use operate by imposing one or more simple stresses on the cord and measuring the time or the number of cycles required to produce cord failure. Although all of them have been able to detect differences among cords, none has reported a quantitative correlation with tire fleet tests. In view of this deficiency, the value of any fatigue test in predicting the fatigue life of a given type of cord in tires may be questioned because there is no proof that the mechanism operating to cause fatigue in the tester is the same as the one operating in tires.

The investigation described in this paper overcomes these objections by analyzing cords from fatigued tires in order to determine what physical changes take place as a result of fatigue and by developing a laboratory testing procedure that fatigues cords in the same manner as tires, using the restriction that the laboratory test produce the same physical changes as were found in tires. The investigation was directed principally at passenger tire fatigue which is less complicated by heat than truck tire fatigue.

ANALYSIS OF CORDS FROM FATIGUED TIRES

Experimental Techniques.—The cords studied were obtained by removing them singly from fatigued tires beginning with the innermost (first) ply. Additional studies were made on the separated yarns and single filaments taken from these fatigued cords. All cords tested were composed of two yarns plied together; the yarns were obtained by separating the cords into the two yarns without changing the final yarn twist. Single filaments were obtained by removing all twist from the yarn and removing the filaments individually.

Tensile tests were made on the cords and yarns using a Scott IP-4 tester operating at a rate of loading of 16 grams per denier per minute at 75° F and 60 per cent relative humidity. In order to overcome a large number of clamp breaks, the samples were snubbed. The clamp spacing was adjusted so that the tensile tests were performed on either the entire length of the cord, *i.e.*, from

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 4, pages 796-800, April 1953. This paper was presented at the semiannual meeting of the Division of Rubber Chemistry, American Chemical Society, Buffalo, N. Y., October 29-31, 1952.

TABLE I
OVEN DRY STRENGTH OF CORDS

Material	Construction	Oven dry strength (kg.)	
		Original calendared cord	Cord from 1st ply after 40,000 miles on test car
Rayon	1650 denier, 2 ply, 11.5 \times 10 twist ^a	12.30	6.82
Rayon	1650 denier, 2 ply, 12 \times 12 twist	11.82	8.64
Rayon	1650 denier, 2 ply, 13 \times 13 twist	11.36	9.87
Cotton	11.5 S/4/2	8.42	6.03

^a A twist of 11.5 \times 10 means 11.5 turns/inch of twist in the ply and 10 turns/inch in the reverse direction in the cord.

bead to crown, or on a short sample length which lay in only one region of the tire.

A study of the torsional stiffness of single fibers was made using the technique of Koch². The method consisted of twisting a single fiber, 1 cm. in length, in a twist counter until it ruptured. Single fibers were mounted on stiff paper such that the 1-cm. length to be studied was centered over a 1-cm. square and was affixed at its edges with adhesive tape. The paper was mounted in a twist counter and the sides perpendicular to the single fiber were cut, thus permitting the single fiber to be twisted. The twist counter was motor driven at 120 r.p.m. Tests were performed at 75° F and 60 per cent relative humidity.

Each fiber was mounted without tension, and before twisting all crimp was removed by elongating the movable clamp in the twist counter. The length of each fiber was measured after crimp was removed, and the twist was corrected to a 1-cm. fiber length.

The degree of polymerization (D.P.) was studied in fatigued cords by measuring the intrinsic viscosity of cellulose in cupriethylenediamine solution. The technique used was to select cord segments which were located in the same ply and region of a fatigued tire. For example, all segments in one analysis would be from the crown of the first ply of a tire. These segments, approximately 1 gram in weight, were then ground in a Wiley mill using a 40-mesh screen along with 100 grams of dry ice to prevent any lowering of D.P. Cords from a new tire were found to have a D.P. of approximately the same value as the original rayon, indicating that there is little loss in D.P. by this technique.

The samples were then dissolved in cupriethylenediamine solution, and all rubber and foreign matter were filtered off and weighed. The intrinsic viscos-

TABLE II
MANUFACTURERS' DATA ON TIRES TESTED
(Cord construction, 1650 denier, 2 ply, 12 \times 12 twist)

Code	Manu- No. factory	Type of tire	Testing conditions			Type failure	Cord used
			Mileage	Overload (%)	Under inflation (%)		
A1	X	4 ply	6,505	29	14	Puncture	du Pont rayon
A2	X	4 ply	20,657	29	14	None	du Pont rayon
B1	X	4 ply, 8.00-15	15,501	21	8	None	du Pont rayon
B2	X	4 ply, 8.00-15	20,000	21	8	None	du Pont rayon
B3	X	4 ply, 8.00-15	31,196	21	8	None	du Pont rayon
C1	Y	4 ply, 6.00-16	Unknown	Unknown	Unknown	Fatigue	Rayon
D1	Y	10 ply, 11.00-22	Unknown	Unknown	Unknown	Fatigue	Rayon
E1	Z	8 ply, 9.00-20	New	—	—	—	du Pont rayon

ity values were determined graphically from the reduced viscosities of cellulose solutions of 1.0, 0.5, 0.25, and 0.125 per cent.

Abrasion in fatigued fibers was studied by the Congo red staining technique³. The fibers were swollen for 3 minutes in caustic, washed in warm water, dried, and immersed in 2 per cent Congo red solution for 1 minute. After washing and drying, the fibers were observed microscopically.

Experimental Results.—Tire cords are known to lose strength with running⁴. The Dunlop Rubber Company⁵ found a marked strength loss in rayon cords from the first ply (i.e., inside ply) of tires run 40,000 miles on the road and removed unfailed (see Table I).

The data show that the amount of strength lost by cords depends on their twist; the lower the twist the greater the strength loss. Cotton had a rate of strength loss comparable to high twist rayon cords.

This information pointed to the possibility of using cord tensile strength as a measure of fatigue. Several manufacturers furnished tires fatigued on road tests for the study. The tires are listed in Table II. Tires A1 and A2 were

TABLE III
CONDITIONED CORD STRENGTHS IN PLYS OF FATIGUED TIRES

Ply ^a	Tire A2		Tire C1	
	Strength (kg.)	Breaks in flex zone (%)	Strength (kg.)	Breaks in flex zone (%)
1	6.73	87	5.41	80
2	7.01	81	7.05	79
3	7.21	50	—	—
4	7.31	13	—	—

^a The plies are numbered from the inside of the tire carcass outward.

fleet tested under the same conditions; they were run different mileages before removal. Tires B1, B2, and B3 were also run under fleet test conditions. Tires C1 and D1 represent a failed passenger and truck tire, respectively. Tire E1 was a new tire.

The first problem studied was the relative cord strength in the various plies of a fatigued tire. In Table III the conditioned cord strength and the number of cords breaking in the flex zone are given for the various plies of tires A2 and C1 which were obtained from different manufacturers. The flex zone is a narrow region in the tire sidewall above the shoulder which undergoes the sharpest bend when a tire is deflected. In this paper, it will be considered arbitrarily to be 1 inch in length along the cord. The cord sample lengths tested were from the bead to the center of the crown.

The data show that cords from the inner ply have lost the most strength and that the weakest point of most of these cords is in the flex zone, which represents only about 12 per cent of the cord length. These findings are in line with tire company experience that the inner ply is the first to fail in flex breaks⁴. It clearly associates cord strength loss with tire fatigue.

In the case of tire C1, a failed passenger tire, all cords tested from the first ply had strengths close to 5.41 kg., even adjacent to the break. Presumably, tires of this construction fail when the average cord strength is in the range of 5 kg. When one point of a cord is weakened to this degree, any elongation of the cord is restricted to this region, resulting in rapid failure.

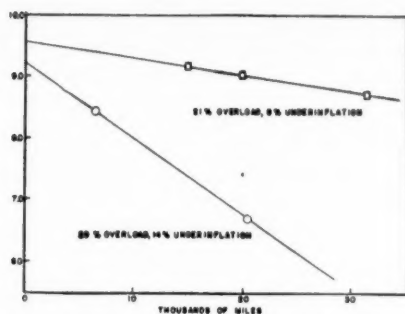


Fig. 1.—Effect of mileage on first ply tire cord tensile strength. 1650/2, 12 × 12 rayon cords

Two series of fleet tested tires were studied to see how first ply cord strength varied with running. The results, shown in Figure 1, point out that loss in first ply cord strength is approximately linear with running. The rate of strength loss, naturally, is a function of the testing conditions. Tires A1 and A2, run at 29 per cent overload and 14% underinflation, lost strength more rapidly than did tires B1, B2, and B3, run at 21 per cent overload and 8 per cent underinflation.

Having shown that fatigue failure stems from progressive loss of cord strength in the flex zone, the analysis was extended to include a comparison of the strengths of cords, yarns, and single filaments from various regions of fatigued tires. In Table IV are shown the results of such a study on a fatigued, unfailed tire, A2. The percentage strength loss is shown based on the original strength of the cords, yarns, and single filaments tested under the same condi-

TABLE IV
STRENGTH LOSS OF FATIGUED TIRE

Region	(Tire A2) Strength loss (%)		
	Cords	Yarn plies	Single filaments
Flex zone	32	55	18.5
Crown	16	29	17.4
Bead	—	—	15.4

tions. The results point out that cords and yarns are weakest in the flex zone, which is in agreement with the data in Table III, which showed that a large percentage of first ply cords broke in the flex zone. The single filament data, on the other hand, did not show this marked weakening in the flex zone; rather, all fibers appeared to lose some strength with running.

These results point to the selective weakening of cords in the flex zone being due to broken filaments. The broken filaments cause an even greater relative strength loss in the yarns, since the yarns contain less twist. In yarns, because of their looser construction, the weak spots caused by broken filaments are not covered up; therefore, yarn strength loss is relatively larger than in the more highly twisted cord construction.

The single filament tests were made on fibers that had not been severed during fatiguing. As a consequence, these results could be biased in showing higher strengths than the true mean filament strength in the region. However,

the significant fact is that the single fibers in all three regions showed approximately the same loss of strength, which is different from the yarn and cord data. Therefore, it was concluded that the yarns and cords were weakened selectively in the flex zone primarily from the higher incidence of broken filaments in that region. Since the single filament studies were made on specimens only $\frac{1}{2}$ inch long, no precise measurement of breaking elongation could be made. If a change in fiber-breaking elongation occurred as a result of fatigue, it was not large enough to be detected.

The over-all loss in filament strength throughout the tire was thought to be due to heat degradation. If such were the case, then the cellulose degree of polymerization would be lowered, with the lowest value at the point in the tire where maximum heat was developed. Measurements of intrinsic viscosity as a function of cord location were made to confirm this hypothesis. The results, shown in Table V, are listed in terms of intrinsic viscosities rather than cellulose D.P., since there is no general agreement at present on the value of the constant to be used in converting intrinsic viscosities into D.P. values.

The intrinsic viscosity results follow the single fiber strength data closely in that all cords from fatigued tires showed a lower intrinsic viscosity than cords from a new tire. Both Lewis⁶ and Conrad, Tripp, and Mares⁷ demonstrated

TABLE V
INTRINSIC VISCOSITY AS A FUNCTION OF CORD LOCATION

Region	Intrinsic viscosity			
	Tire A2, fatigued passenger	Tire C1, failed passenger	Tire D1, failed truck	Tire E1, new
Crown	2.01	2.02	1.89	2.16
Shoulder	1.93	1.98	1.65	—
Sidewall	1.98	—	1.87	—
Flex zone	2.03	2.02	1.75	2.22
Sidewall	2.03	—	1.82	—
Bead	2.02	1.90	1.85	2.04

that heating of cotton and rayon cords lowered both the D.P. and the tensile strength. The data in Table V show that the lower D.P. was more or less uniform throughout the tires, except tire D1, a failed truck tire, where the shoulder had a significantly lower intrinsic viscosity than other regions. These measurements on cords from passenger tires suggest that the over-all loss in single fiber strength is attributable to heat degradation.

Although the single fiber tensile tests could not distinguish between flexed and unflexed fibers, it was found that flexing did change the extent to which single fibers could be twisted without rupture. Koch² used this technique in determining the stiffness of different types of fibers. Koch compensated for mass and area differences by calculating the breaking twist angle, using the equation:

$$\tan \alpha = \frac{267.4}{DB} \sqrt{\frac{S}{T_d}}$$

where

- α = breaking twist angle
- DB = turns of twist per cm.
- S = fiber specific gravity
- T_d = gauge, in denier

Since all fibers in this study had the same specific gravity and average denier, the breaking twist per cm. of the fibers was directly comparable. Shown in Table VI are the results of breaking twist experiments on single filaments removed from the inner ply of three passenger tires.

Although the agreement among tires is not too good, in each case the flexed region had a lower breaking twist. This study indicates that fatiguing causes fibers to become more sensitive to torsional stresses.

The single fiber tensile results indicated that abrasion was not a major cause of fiber failure in the flex zone since abrasion would cause all fibers in that zone

TABLE VI
TESTS ON SINGLE FILAMENTS

Tire	Fiber breaking twist (turns/cm.)		
	A2	B3	C1
Flex zone	94	96	109
Bead	108	100	114

to be weaker and this was not the case. A further check on the incidence of abrasion was made, using the Congo red dyeing technique³. For the cords studied, no evidence of abrasion of fibers was present. For abrasion to be a major factor in passenger tire flex fatigue, it would have to be present to a large extent in the flex zone of the first ply cords of tire C1, which had lost half its original cord strength, yet none was found.

FATIGUE TESTING

The analysis of tires demonstrated that linear loss in cord strength is intimately associated with cord fatigue in tires. Therefore, a useful criterion for evaluating fatigue testers is the study of cord tensile strength while running on the testers.

Experimental Procedure.—In this study, four different testers were investigated: the U. S. Rubber constant stretch tester⁹, the du Pont dynamically balanced tester¹⁰, the Goodyear compression tension tester¹¹, and the Goodrich compression fatigue tester¹², a disk-type tester which operates by stressing the cord between two rapidly rotating disks. Since the operating conditions may vary with these testers, a description of their principles of operation and the actual testing conditions used follows:

1. *U. S. Rubber fatigue tester.*—This is an extension-type test in which the instrument cyclically elongates and relaxes cords until they fail. The cords never completely relax, since they continuously sustain an applied load. The tester contains an automatic take-up device to compensate for growth, thus the cords always undergo the same per cent extension. The tester was operated with a 30-inch specimen elongated 1.70 per cent while under a load of 0.14 grams per denier, running at 360 cycles per minute at 65° C and 7 per cent relative humidity.

2. *du Pont dynamically balanced tester.*—This tester also operates by alternately stressing and relaxing cords until they fail under the applied load. In this test, two cords supporting a weight are alternately stretched and relaxed by two eccentrics located 180° out of phase with respect to each other on a common rotating shaft. As one cord is being stretched, the other is relaxing. Since the total stress remains constant, the load does not attempt to follow the eccentrics. This tester fatigues a 16.75-inch sample by elongating it cyclically

1.44 per cent at 3000 cycles per minute while under a load of 1.0 gram per denier. The tester is operated at 100° C and 1.5 to 3.0 per cent relative humidity.

3. *Goodyear compression tension tester.*—The Goodyear tester is an "in rubber" test which causes the cords to be alternately compressed and extended. The test consists of building a rubber tube 2.75 cm. in width and 25 cm. long in which cords are embedded longitudinally in the rubber. When placed on the tester, the tube is bent through an arc of 90° and rotated at a speed of 850 r.p.m. Air is introduced into the tube when it is on the tester to keep it inflated in a uniform arc and to provide a stress, which causes the cords to fail. In this work, two test cycles are used: the first consisted of a half hour of operation at 20 pounds per square inch internal air pressure, followed by 2 hours of

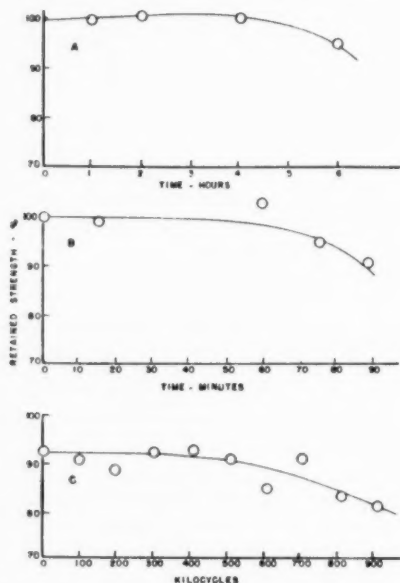


FIG. 2.—Per cent cord strength retained in fatigue tests. A. U. S. Rubber fatigue test⁴. B. Du Pont dynamically balanced fatigue test⁵. C. Goodyear compression tension test, using 50 lb./sq. inch pressure cycle.

operation at 25 pounds per square inch and subsequent increases of pressure of 5 pounds per square inch every 2 hours to failure of the tube; the second consisted of a half hour of operation at 20 pounds per square inch, followed by a constant pressure of 50 pounds per square inch until the tube failed.

4. *Goodrich compression fatigue tester.*—This is an "in rubber" test in which single cords are embedded in black rubber blocks $3 \times 7/16 \times \frac{1}{2}$ inches. The blocks are mounted between two parallel disks spaced 1 inch apart. Prior to starting the test, one of the disks is canted with respect to the other, causing the disks to be closer together on one side of the tester and farther apart on the other. Thus, when the disks revolve, the rubber block is alternately compressed and extended.

TABLE VII
CORD FAILURE

Tester	Testing conditions		Cycles to failure
	Extension max. (%)	Compression max. (%)	
U. S. Rubber	2-6 ^a	0	220,000
du Pont dynamically balanced	5 ^b	0	210,000
Goodyear compression tension	4	17	700,000
Goodrich compression fatigue	5	5	2,000,000
Passenger tires (14)	2	6-15	20,000,000-40,000,000

^a U. S. Rubber tester actually produces much greater cord elongations than the 2% stretch cycles because considerable creep takes place due to the automatic take-up device during the test life of the sample. Before failure, cords are elongated 6% or more (1).

^b The 5% extension refers to the original elongation. Creep occurs during running.

The shafts which hold the disks are mounted on movable plates so that the tester can be run at any desired compression and extension. The blocks were not run to the point of cord failure, but instead were run for a specified time and removed unfailed. The cords were then removed from the blocks by cutting away the rubber. Repeated tests have shown that this can be done without degrading the cords. After removal from the blocks, the cords were tensile tested on a Scott IP-4 tester at a rate of loading of 16 grams per denier per minute. The tester was run at a speed of 1600 r.p.m. in an atmosphere at 75° F and 60 per cent relative humidity.

Experimental Results.—Cords run on these four testers were studied to see if they showed a loss of strength with running comparable to that observed in fatigued tires. Graphs of retained strength vs. test life for the U. S. Rubber, du Pont, and Goodyear tests are shown in Figure 2. The curves show that the strength loss is not linear and that after 90 per cent of the test has been completed, the cords retain 80 per cent or more of their strength. A similar effect occurred in the fatigue tester developed at the Southern Regional Research Laboratories and reported by Grant, Couturier, and Rhoades¹³. They found that rayon cords lost only 3 per cent of their tensile strength after 57 per cent of the test had been completed.

The fact that these testers do not fatigue cords in the same way as tires is not surprising, since they all operate under severe testing conditions so far as the magnitude of the imposed strains is concerned, causing cords to fail much

TABLE VIII
EFFECT OF TWIST ON FATIGUE RESISTANCE

Twist	Initial conditioned strength (kg.)		Strength Loss (g./ 1,000,000 flexes)	
	Dunlop tire data	Goodrich disk-type tester	Dunlop tire data	Goodrich disk-type tester ^a
9 × 9	—	11.20	—	820
11 × 11	10.32	10.24	163	270
12 × 12	9.90	9.78	99	59
13 × 13	9.33	—	42	—
Cotton 11.5 S/4/2	7.82	8.43	83	100

^a Run under conditions of 15% compression, 3% extension.

more rapidly than they do in tires, as shown in Table VII. The extension and compression values refer to the changes in length along the cord axis.

All these tests show the same strength loss picture in that they cause cords to fail much more rapidly than in tires, and all subject the cords to greater extensions than are found in tires. Further, all tests cause cotton cords of comparable denier to fail much more rapidly than low twist rayon cords.

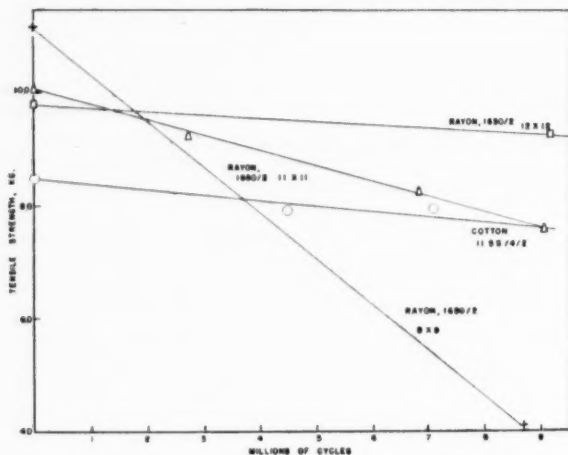


Fig. 3.—Goodrich disk-type test of cord fatigue.

Laboratory testers would have a more tire-like fatiguing action if the degree of cord extension and compression were brought closer to that found in tires.

Studies were made with both the Goodrich and the Goodyear tester, run under conditions simulating tire strains, in order to check this hypothesis. Since the Goodrich disk-type tester permitted a closer control over the degree

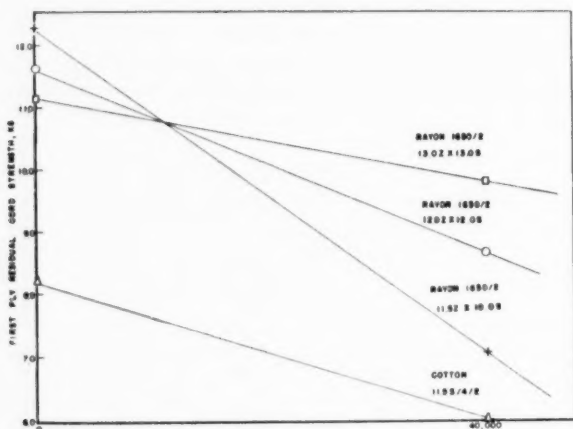


Fig. 4.—Dunlop tire test. Oven-dry results. Tires removed, unfailed, after 40,000 miles

of extension and compression than the Goodyear tester, it was used in most of the studies reported here.

The disk-type tester, when operated under conditions of 3 per cent extension and 15 per cent compression, was found to duplicate tire fatigue data in that cord strength decreased linearly with running, and cotton cords were rated correctly with respect to rayon cords. Also, the relative rate of strength loss of rayon and cotton was similar to that found in passenger tire fleet tests. This is the first time a laboratory tester has been reported which rates cotton and rayon rates of strength loss in the same way they are found in passenger tires.

The Dunlop tire data indicate a strong dependence of rate of strength loss on cord twist, which is also observed in the Goodrich tester run under these conditions. Both show that increasing twist results in a more fatigue-resistant cord. These data are tabulated in Table VIII and shown in Figures 3 and 4. The cords in both tests were made from the same type of yarn. The original Dunlop data shown in Figure 4 were taken on an oven dry basis. In Table VIII they have been corrected to bring all data to a 12 per cent moisture regain basis. In the case of the tires, it was assumed in Table VIII that each tire revolution caused the cords to go through one flexing cycle, or that in 1500 miles the cords were flexed approximately 1,000,000 times.

TABLE IX
RATE OF CORD STRENGTH LOSS ON GOODRICH TESTER

Testing conditions		Strength loss (g./1,000,000 flexes)
Compres- sion (%)	Exten- sion (%)	
0	3	30
2	2	0
15	0	65
15	2	115
16	2	180
15	3	270

Under the testing conditions used, the Goodrich tester appears to be more sensitive to differences in cord twist than was found in the tire study. By changing testing conditions, the rate of cord strength loss with running is markedly affected. This is shown in Table IX.

These data show that high rates of fatigue do not take place until the cord is subjected to both a compression and an extension. This finding is in agreement with the finding in tires that the inner ply is the most severely fatigued¹. The inner ply is subjected to the largest compression, although it is not subjected to as large extensions as the other plies.

TORSIONAL STIFFNESS

Just as in tires, it was found that fibers taken from the flexed region of the rubber block samples used in the Goodrich disk-type tester had a lower breaking twist than fibers taken from the unflexed region. (The unflexed region was considered to be that portion of the cord under the clamps in the tester.) For 1650 denier, 2 ply, 11 × 11 twist rayon cords, fibers from the flexed region had a breaking twist of 76 turns per cm. compared to 109 turns per cm. for fibers from the control region.

SUMMARY

Fatigue in tire cords causes a linear loss of cord tensile strength with mileage and an increased fiber torsional stiffness. The loss in cord strength is centered mainly in the flex zone. The loss of cord strength stems from broken filaments and from a small loss of fiber strength throughout the tire. The lowered fiber strength is attributed to a lowered D.P., and does not appear to be connected with the broken filaments observed in the flex zone. The cause of the broken filaments has not been resolved. However, studies show that it is not due to abrasion or heat degradation.

It was found possible to duplicate tire fatigue characteristics in the laboratory by causing cords to go through an extension-compression cycle approximately equivalent to the one in tires. Under these conditions, the Goodrich disk-type tester showed the same relative rate of strength loss for rayon and cotton cords as was found in a passenger tire fleet test.

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EVALUATION OF OZONE PROTECTIVE AGENTS FOR ELASTOMERS

APPARATUS FOR THE EVALUATION UNDER DYNAMIC CONDITIONS *

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Exposure cracking has been evidenced to various degrees by the majority of elastomers under strain and has presented a serious service and appearance problem for many years. Its cause has been attributed to many factors—light, oxygen, ozone, heat, and moisture. Newton¹ clarified the situation and showed that ozone was the major cause of exposure cracking.

With the widespread acceptance of GR-S for use in rubber goods, the need for a protective agent effective against ozone has become more pressing, as GR-S appears to be more susceptible to ozone attack than the natural rubber which it replaced². Waxes³ oxidized rubber⁴, cellulose⁵, and bituminous paint⁶, which prevented ozone from reaching the rubber surface, have been cited in the literature, and in some cases employed commercially as a means of reducing this cracking in articles where static or even mild flexing conditions prevailed. For these, a static method of evaluation⁷ appeared to be satisfactory. During the past few years, several compounds have been reported which provided protection under dynamic conditions; however, these were found to be unsatisfactory because of their toxicological or deleterious aging properties.

DEVELOPMENT BACKGROUND

At the time this program was instigated, two instruments were readily available for evaluating the surface cracking of stocks under dynamic conditions: a flexer developed by Throdahl⁸ to study the surface cracking in GR-S exposed to ultraviolet light and a belt flexer utilized by the Monsanto Chemical Company's Technical Service Laboratories in Akron, Ohio, for studying ozone cracking. The belt flexer consisted of a canvas belt suspended over pulleys to which $\frac{1}{4} \times 2 \times 4$ inch test-slabs were vulcanized. Flexing was obtained as the belt passed over the pulleys. This type of apparatus has been employed by the soling industry to evaluate the flex characteristics of shoe soles. For studying ozone cracking, the belt mechanism was enclosed in an ozone chamber.

A modification of the ultraviolet light flexer proved unsatisfactory because with the use of higher amounts of ozone (25 ± 5 parts per 100,000,000 parts of air) the strips cracked so severely within a few hours that the sensitivity of the method was lost. The belt type of flexer was found to meet the needs and provided the additional advantage of simplicity of construction.

Originally, circles died from standard stress-strain sheets were employed. Considerable difficulty was encountered in the visual evaluation of the cracking

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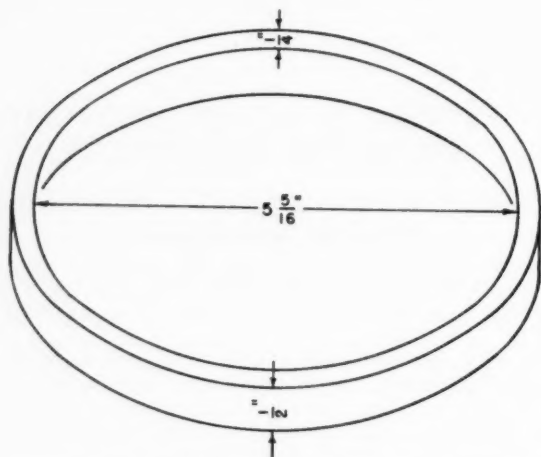


FIG. 1.—Isometric sketch showing dimensions of molded, circular, belt-type test-specimens used in conjunction with dynamic ozonizer.

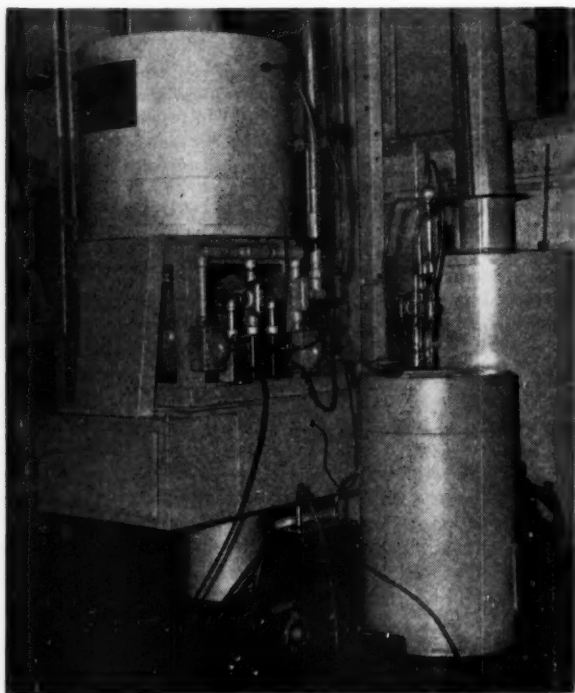


FIG. 2.—Dynamic ozonizer. Chamber in position and ozone analysis apparatus.

because of the variation in the size of the cracks. A thick specimen was adapted after inspection of a number of Ross flexer slabs from the Phillips Petroleum Company's Laboratories in Akron, Ohio. These slabs, 0.25 inch thick, offered a big advantage over the thin specimens, in that they showed a uniform size of surface crack, they were large enough so that the degree of cracking was easily determined by visual means, and they were easy to handle. Therefore, a thick molded circular belt-type of test-specimen measuring $\frac{1}{2}$ inch wide, $\frac{1}{4}$ inch thick, and 5% inches in diameter was developed. An isometric sketch of the test-specimen is shown in Figure 1.

DESCRIPTION OF DYNAMIC OZONIZER

A photograph of the dynamic ozonizer is shown in Figure 2. The operation of the apparatus is indicated in Figure 3.

An ozone concentration of 25 ± 5 parts per 100,000,000 parts of air is generated by a Hanovia burner, *O*. Baffles at the top and the bottom of the chamber protect the personnel from the ultraviolet light, but do not restrict the air flow. The production of ozone is controlled manually by means of Variac *V* through a 15,000-volt transformer. The ozonized air passes through duct *D* to the chamber. The circular test-specimens, *B*, are supported on a series of

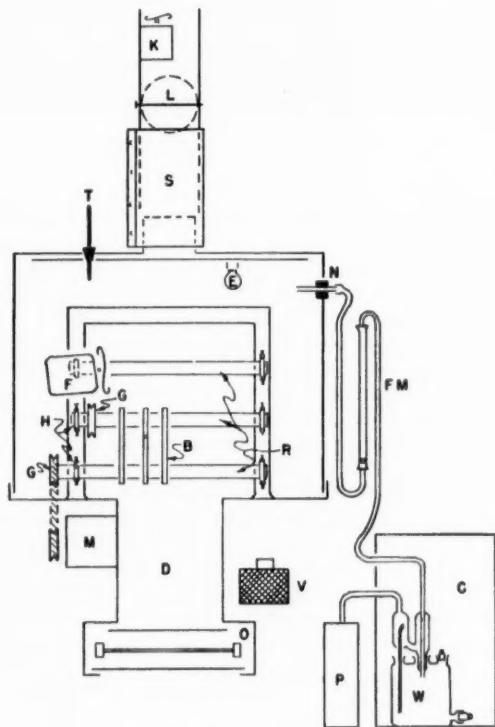


FIG. 3.—Diagrammatic sketch of dynamic ozonizer.

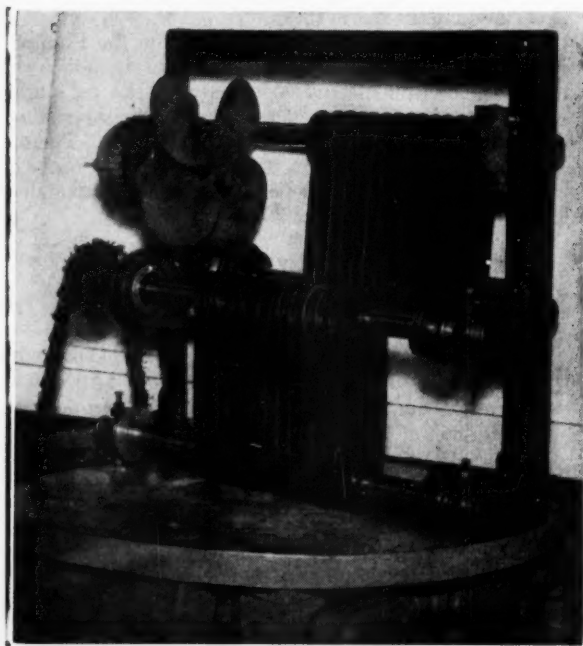


Fig. 4.—Construction and position of rolls and mounting of test-specimens.

1-inch rotating stainless steel rods, *R*, which in turn are mounted on an iron frame by means of pulley hangers, *H*. The rods are rotated by a 2.5-inch pulley *G*, connected through a V-belt to a $\frac{1}{4}$ hp. motor, *M*. As any portion of test-specimen passes over the rolls, a momentary elongation through a range of 0 to 20 per cent is provided. This flexing is at a rate of approximately 75 flexes per minute. The present apparatus consists of two such series of rolls, upon which 36 specimens may be exposed at the same time (Figure 4). Uniformity of the ozone-air mixture is ensured by the use of the fan, *F*, mounted on the frame. The rate of flow (35 cubic feet per hour or 1 cubic meter per hour) is regulated by means of a louver, *L*, in the stack in conjunction with a fan, *K*. The louver is adjusted so that a constant ozone concentration of 25 ± 5 per 100,000,-000 parts of air is maintained in the chamber.

The uniformity of the ozonized air is shown in Table I.

An array plot of the ozone concentration over an extended period of time is shown in Figure 5. As may be seen, the addition of the stack and the vent fan

TABLE I
OZONE CONCENTRATION IN VARIOUS PARTS OF THE DYNAMIC TESTER

	Parts per 100,000,000
At sampling outlet side	26.3
Opposite side	26.6
Top below vent stack	29.4
Center of frame	23.4
Composite side and top	29.4

has a marked effect in maintaining a uniform and consistent atmosphere. No attempt is made to control the air temperature, but an average temperature of 30° C is usually maintained.

The ozone concentration is determined twice daily by the conventional potassium iodide method of Crabtree and Kemp⁷. Samples of air are drawn from the chamber at *N* by application of a vacuum (Welch Duo-Seal pump), *P*, to the Woulff bottle, *W*, and the flow is measured by a standard Porter-Fisher flowmeter, *FM*. The Woulff bottle and reagents are enclosed in a light-tight container, *C*, to prevent the photochemical decomposition of the potassium iodide.

Other methods of ozone analysis have been considered, but none provides the accuracy and practicability of the potassium iodide method.

RATING SYSTEM

In order to have some means of selecting promising ozone-protective agents and to aid in a general cross-comparison between experiments, a rating system was deemed necessary. Because the instrument was to be utilized for screening purposes, any system adopted should be able to distinguish between small differences in effectiveness and be simple enough so that nontechnical personnel could rate large numbers of compounds accurately and rapidly without expensive or elaborate equipment.

An arbitrary rating system was devised because none of the systems described in the literature appeared to meet the requirements. A direct means of rating such as that proposed by Rugg⁹ required elaborate expensive equipment, necessitated the destruction of the specimen, and was slower than other meth-

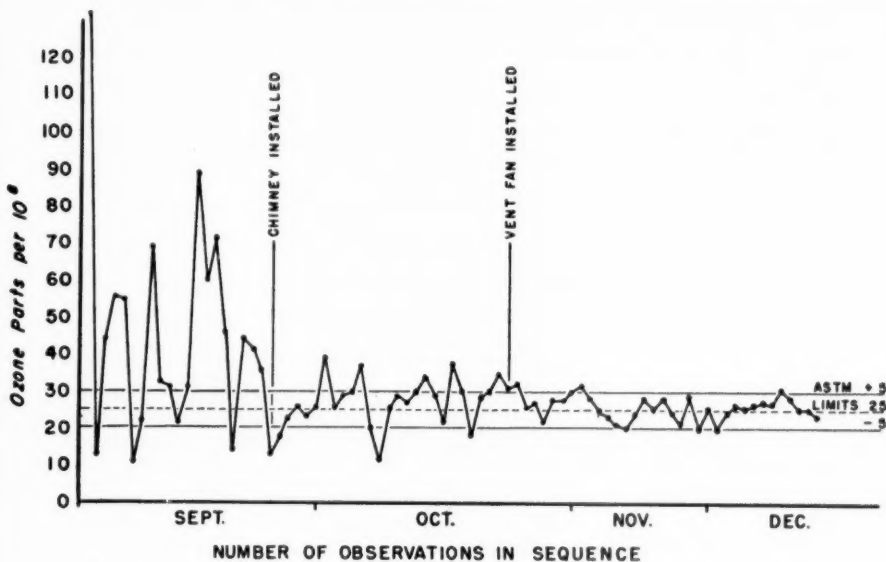


FIG. 5.—Array plot of ozone concentration in chamber over an extended period of time. Analysis employed conventional potassium iodide method. ASTM limits of 25 ± 5 parts are designated.

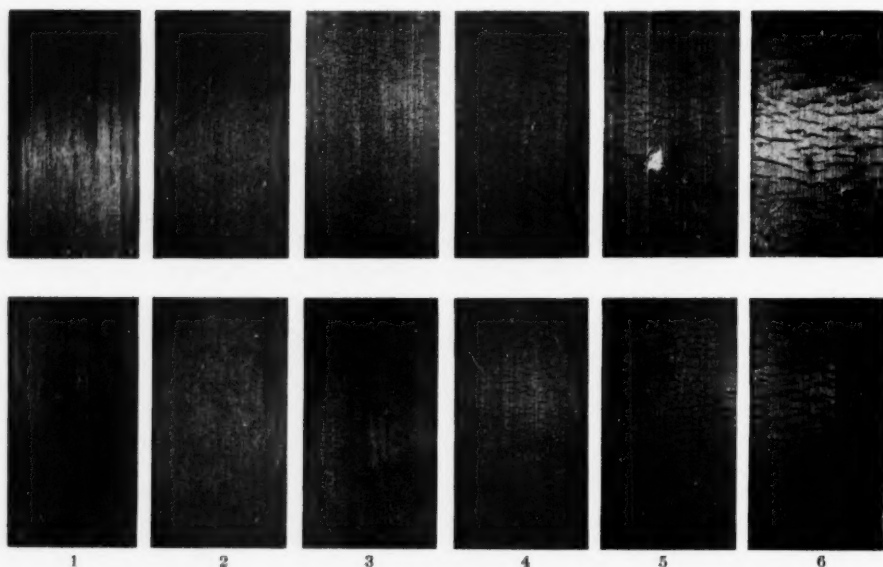


FIG. 6.—Standard reference series for ozone cracking in Hevea and GR-S HAF tread stocks. Upper series, GR-S; lower series, natural rubber. Rating numbers illustrate following severity of cracking: (1) no cracking; (2) very slight cracking; (3) slight cracking; (4) moderate cracking; (5) severe cracking; (6) extremely severe cracking. 10 \times magnification.

ods. The objection to indirect systems which relate known physical properties to the extent of ozone cracking¹⁰ was that other degradative influences encountered in aging might affect the properties being evaluated. Newton's rating system¹¹, which relates standard cracking to hypothetical cracking is rather indirect, allows many chances for error, and is in general too complex for rapid use.

A simple, accurate, and rapid means of rating was devised in the following manner. First, a series of standards covering the range of cracking desired for study was prepared. Six specimens each of Hevea rubber and GR-S were employed. Five of these were exposed in the ozone chamber until examples of very slight, slight, moderate, severe, and extremely severe cracking were obtained. The standard series for Hevea rubber and GR-S tread stocks are shown in Figure 6. An arbitrary rating of 1 was assigned to the sample with no cracking and 6 to the one with extremely severe cracking. The others were given appropriate ratings in between these extremes.

The experimental test-specimens were visually compared at intervals (usually 24 hours) with the standards and were assigned a rating which was indicative of the extent of cracking at the time. This provided a measure of the effectiveness of a given material over a period of time and showed the approximate time for initial cracking. For the sake of clarity, typical examples of each step are shown.

Stock	Rating numbers at 24-hour intervals					
	1	2	1	4	6	6
1	1	1	1	1	1	1
3	1	1	1	1	1	1
13	1	1	1	2	3	3

To obtain a picture of the over-all effectiveness of any compound and to magnify small differences, the ratings were interpreted mathematically in the following manner. Arbitrary values of 0, 2, 4, 8, 16, and 32 were assigned to the ratings (32 to 1, 0 to 6).

Rating no.	Value
1	32
2	16
3	8
4	4
5	2
6	0

These were substituted for the ratings and totaled:

Stock							Total
1	16	16	4	0	0	—	36
3	32	32	32	32	32	32	192
13	32	32	32	16	8	8	128

In their work the authors utilized a stock containing 3.0 parts of Santoflex-AW per 100 parts of rubber as a control to which all the exploratory materials were compared. The totaled values were, therefore, divided by the total for Santoflex-AW and multiplied by 100. This gave an arbitrary rating in which all stocks were comparable on the basis of 3.0 parts of Santoflex AW as 100.

$$\frac{36}{192} = 0.18 \quad 0.18 \times 100 = 18 \quad (1)$$

$$\frac{192}{192} = 1.00 \quad 1.00 \times 100 = 100 \quad (2)$$

$$\frac{128}{192} = 0.66 \quad 0.66 \times 100 = 66 \quad (3)$$

As the ratings of the specimens depended on the personal judgment of the three observers, it appeared desirable to determine the reliability and consistency of their evaluations. Twenty stocks of both Hevea rubber and GR-S having previously assigned ratings ranging from 1 to 6 were rated by each person independently three times in a random order, so that they were unaware of their previous ratings. A statistical analysis of the results showed an over-all 10 per cent error of ± 1 rating unit. The average per cent error for each observer ranged from 7.6 to 12. The probability of a ± 2 rating unit error was negligible. This is graphically illustrated in Figure 7.

TEST RESULTS

The experimental screening program has been restricted to the use of two elastomers, Hevea rubber and GR-S.

In order to reduce the experimental variables to a minimum, a standard procedure for milling and curing was adopted. Typical Hevea rubber HAF black and GR-S HAF black tread stocks having the compositions shown in Table II were utilized as test recipes.

This apparatus and rating system appeared to provide a good means of evaluating and rating ozone protective agents. In Hevea rubber and GR-S tread stocks of the above formulations, the effect of 0.4 per cent increments of

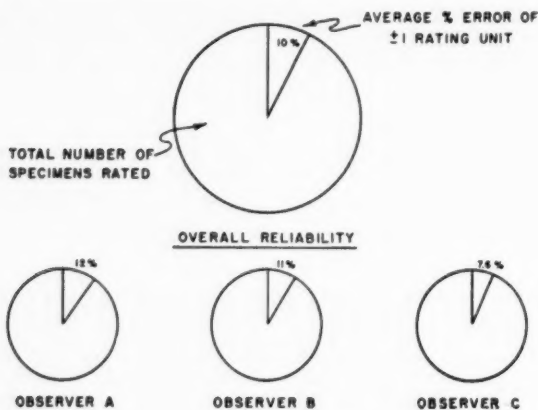


Fig. 7.—Reliability and reproducibility of rating evaluations for three observers and over-all reliability of method. Percentage error of ± 2 rating units was negligible.

TABLE II
STOCK FORMULATIONS EMPLOYED IN EVALUATION PROGRAM

Compounding ingredients	Base A	Base B
Hevea as smoked sheet	100.0	—
GR-S 100 (low temperature polymer)	—	100.0
Furnace black (Philblack-O)	50.0	40.0
Furnace black (Philblack-A)	—	10.0
Softener (Paraflux)	3.0	10.0
Zinc oxide	5.0	4.0
Stearic acid	2.0	2.0
Sulfur	2.5	1.75
<i>N</i> -Cyclohexyl-2-benzothiazole sulfenamide	0.8	1.2
Ozone protective agent	0-3.0	0-3.0

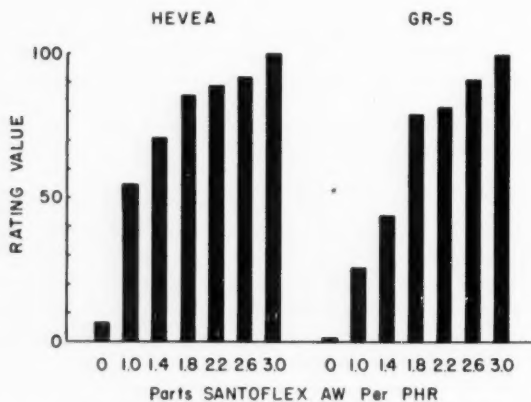


Fig. 8.—Ozone protective action of Santoflex-AW in Hevea rubber and GR-S tread stocks over range of 1 to 3 percent. Based on rating system utilizing 3.0 per cent Santoflex AW as 100.

Santoflex-AW over a range of 1.0 to 3.0 per cent could be readily distinguished, and as little as 1.0 per cent Santoflex-AW produced a marked increase in the ozone resistance of the stocks. However, much better protection was afforded when 3.0 per cent Santoflex-AW was employed. These data are graphically illustrated in Figure 8. Preliminary evaluation indicated good correlation with outdoor tests. Further work to confirm these data is in progress.

SUMMARY

The widespread acceptance of synthetic elastomers for use in rubber products has greatly magnified the problem of obtaining satisfactory protection against weathering in general and ozone attack in particular. Because the tentative ASTM method of evaluation is not entirely satisfactory, a dynamic apparatus has been developed which provides an effective means for accelerated evaluation of ozone protective agents, using a new mechanical arrangement for flexing the rubber, a new specimen shape, rigid control of the ozone concentration, and a new rating system. The apparatus consists of a series of rotating pulleys within a circular chamber. The test-specimens, circular molded belts, are rotated around two pulleys, which gives them approximately 75 flexes per minute with an elongation of 0 to 20 per cent. The flexing provides a mobile surface, so that rigid waxy films cannot be formed, and the molded specimen eliminates the possibility of freak cracking and anomalies due to minute nicks or imperfections during dieing out. The larger surface available for examination facilitates interpretation of results. Air at a rate of 1 cubic meter per hour passes through the chamber with a controlled ozone concentration of 25 ± 5 parts per 100,000,000 at 30° C. Uniformity is ensured by use of a fan in the chamber. The concentration of ozone is determined by potassium iodide method. By a simplified rating system a non-technical person can rate a large number of specimens rapidly and without elaborate equipment.

ACKNOWLEDGMENTS

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AIDS IN VULCANIZATION OF LIGNIN-NATURAL RUBBER COPRECIPITATES

LEAD, COPPER, AND BISMUTH OXIDES *

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The first formulation tried in this compounding study of lignin-natural rubber coprecipitates is shown in Table I. This formulation, No. 1 in the table, would not cure. Lengthening the time of cure or raising the temperature did not help. The acceleration was of the conventional type and consisted of a combination of benzothiazyl disulfide (1.0 part per 100 parts of rubber) and diphenylguanidine (0.4 part per 100 parts of rubber). This behavior was considered surprising, since this accelerator combination is relatively powerful and under certain circumstances, scorchy.

A considerable number of formulations not specifically recorded in this paper were then tried, with little success. Increasing accelerator dosage helped but little. Test-slabs were uncured or undercured, logy, often tacky, with blisters, and could be removed from the mold only with difficulty. Increasing the sulfur dosage did not improve matters appreciably, and such a procedure was of doubtful utility because of the known poor aging characteristics of compounds with high sulfur.

Unpublished data on hand give evidence of similar difficulty experienced by other experimenters in this field.

Keilen, Dougherty, and Cook¹ reported results obtained with coprecipitates of sulfate lignin with natural, nitrile, and Neoprene rubbers. Relatively low sulfur with high accelerator dosage (3 parts of mercaptobenzothiazole plus 1.5 parts of tetramethylthiuram monosulfide per 100 parts of rubber) was used in the natural rubber formulations. These investigators obtained good tensile strength and modulus, and stated that a more intensive search and testing of different curing agents could result in general improvement of properties.

No delay in the vulcanization rate was observed when lignin was added to rubber as a dry powder but, as is well known, this method of addition results in relatively low tensile strengths. It was when lignin was incorporated into rubber by the coprecipitation process that the delayed vulcanization rate was observed.

The coprecipitation process consisted of first mixing together ammonia-preserved natural rubber latex and an alkaline aqueous solution of lignin of pH about 11 in the desired proportion. This mixture was added to a coagulant

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consisting of a 50-50 mixture of sodium chloride and sulfuric acid in aqueous solution. The mixture of latex and coagulant was maintained at a temperature of 90° C during the addition. Further coagulant was added at the same time as the latex to maintain the pH at approximately 2. The coprecipitate thus obtained was filtered, washed, and dried.

Oxidized alkali lignin was used throughout. The oxidized lignin for these experiments was prepared by heating a solution of the sodium lignin salt in water, and bubbling air through this solution. The tendency to turn acid was counteracted by the addition of sodium hydroxide during the oxidation. This solution was then added to the latex for coprecipitation. Other methods of preparation of oxidized lignin are possible as shown by Raff and Tomlinson².

Since it is known that lignin when heated with sulfur reacts readily to form hydrogen sulfide, it was thought that this reactivity might explain the delayed vulcanization rate.

Booth and Beaver³ showed that rubber dissolves 1 per cent of hydrogen sulfide at room temperature and that this amount of gas is sufficient to retard the rate of vulcanization of all types of accelerators.

The formation of hydrogen sulfide during the vulcanization of rubber with sulfur has been observed by many investigators, including Jaworonok⁴ and Okita⁵.

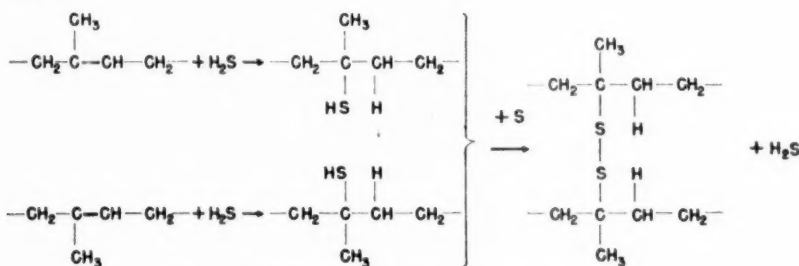


FIG. 1.—Fisher's postulated mechanism of sulfur vulcanization.

Fisher⁶ proposed a theory to the effect that hydrogen sulfide is a necessary intermediate in vulcanization. His postulated mechanism of vulcanization is given in Figure 1. This diagram shows hydrogen sulfide, formed by reaction of sulfur with the hydrocarbon, combining with rubber at the double bonds after splitting up into hydrogen and sulfhydryl. Further reaction with sulfur with evolution of hydrogen sulfide leads to the cross-linking effect necessary for vulcanization. Since hydrogen sulfide is evolved, it is possible that a high concentration of hydrogen sulfide in the medium might slow down the vulcanization reaction through the application of the law of mass action.

The chemistry of vulcanization has, of course, progressed considerably since 1939. Notably, Farmer⁷ brought forth evidence in favor of the theory that sulfur reacts at the α -methylene carbon atom in rubber rather than at the double bond. Since Farmer's theory does not explain the saturation of the double bonds occurring during vulcanization, Bloomfield⁸ showed how this saturation could occur through various possible radical reactions, including the addition of hydrogen sulfide to the double bond.

More recent work on the chemistry of vulcanization by Craig, Juve, and Davidson⁹, Craig, Davidson, Juve, and Geib¹⁰, and Craig, Davidson, and Juve¹¹

brings out the point that hydrogen sulfide is a necessary intermediate in vulcanization, but that when present in excessive amounts it delays vulcanization by acting as a chain terminator. They also regard zinc oxide as a buffer that serves to keep the concentration of hydrogen sulfide down to a level at which vulcanization is not delayed. However, zinc oxide is ineffective in the presence of coprecipitated lignin.

The present work calls attention to the existence of metallic oxides, namely, the oxides of lead, copper, and bismuth, which are the only ones that can control in the proper manner the concentration of hydrogen sulfide during the vulcanization of lignin-natural rubber coprecipitates.

COMPOUNDING EXPERIMENTS

Test methods.—ASTM procedure in the preparation of the rubber samples and in the carrying out of the physical tests was followed.

Formulations.—Table I shows results obtained with a few of the formulations tried in the development of a lignin-natural rubber compound which would cure satisfactorily.

Formulation 1 has already been mentioned. It contains conventional acceleration, which did not cure in the presence of coprecipitated lignin.

The simple addition of 7 parts of litharge per 100 parts of rubber to formulation 1 brought about a remarkable improvement in the result (formulation 2). As shown by the modulus at 300 per cent elongation, a satisfactory cure was obtained. In formulation 3 it is shown that 7 parts of litharge per 100 parts of rubber without zinc oxide cured equally well, although the tensile strength was lower by about 400 pounds per square inch at the longest cure (75 minutes at 292° F) than the formulation with both zinc oxide and litharge.

In formulation 4 the 7 parts of litharge per 100 parts of rubber used in formulation 3 was increased to 10 parts. The principal effect was slight increases of modulus and tensile strength at the 75-minute cure. In formulation 5 the acceleration was changed to zinc dimethyldithiocarbamate. While this did not increase the modulus, both tensile strength and elongation at break were considerably improved.

Although all possible acceleration combinations were not tried, it is evident that the thiocarbamate type of acceleration has a specific beneficial effect. After much experimentation it was decided to retain the zinc oxide and thiazole types of acceleration in the formulation, in addition to litharge and thiocarbamate acceleration, as shown in formulation 6. Apparently zinc oxide carries out its normal function in bringing out the best physical characteristics of the rubber.

Search for other oxides.—The metals whose oxides were effective in bringing about rapid vulcanization of lignin-natural rubber coprecipitates were, as stated, lead, copper, and bismuth. It is thought that these three metals are distinguishable from zinc in the solubility of their sulfides. These three metals have sulfides which are insoluble in dilute acids and in sodium and ammonium polysulfide. Zinc sulfide is soluble in dilute acid and belongs in a different group in the qualitative analysis scheme. This suggests that the three metals effective in the vulcanization of lignin-natural rubber coprecipitates may be characterized by the somewhat greater insolubility of their sulfides.

Many other oxides were tried without success, including those of calcium, magnesium, barium, cadmium, cobalt, manganese, nickel, iron, and others. The fact that such oxides as those of calcium and magnesium are ineffective

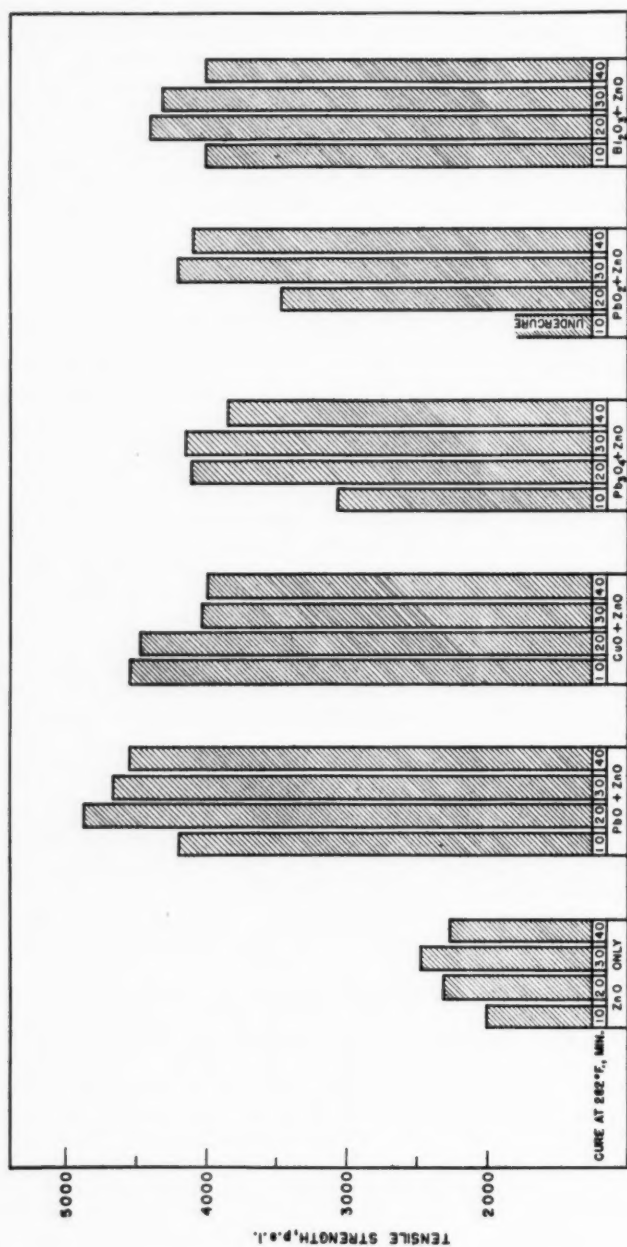


FIG. 2.—Tensile strength bar graphs showing effect of lead, copper, and bismuth oxides in lignin-natural rubber coprecipitate. Formulation 6: 27.8 volumes of lignin, 3 parts of zinc oxide and 7 parts of other oxide per 100 parts of rubber.

TABLE II
FORMULATION 6, FOR COMPARISON OF OXIDES (PARTS)

Natural rubber	72.2
Lignin, 27.8 vol. (coprecipitated)	36.1
Smoked sheet ^a	27.8
Stearic acid	2
Zinc oxide	3
Zinc dimethyldithiocarbamate	1
N-cyclohexyl-2-benzothiazole sulfenamide	0.5
Sulfur	2
Other metallic oxides	7

^a Added to make rubber equal 100.

shows that the delay in the rate of vulcanization of lignin coprecipitates is not due to residual acidity from the coprecipitation, since such oxides would be expected to neutralize acidity.

Comparison of oxides.—Figure 2 shows a comparison of the oxides found satisfactory to date. The compounds compared were made up according to formulation 6, Table II, and all contained zinc oxide. The acceleration was a combination of *N*-cyclohexyl-2-benzothiazole sulfenamide and zinc dimethyldithiocarbamate. Special oxide, added for rapid vulcanization, was used in the proportion of 7 parts per 100 parts of rubber.

Zinc oxide, used alone as a control, showed a relatively low tensile strength of around 2000 pounds per square inch. The modulus, not shown in the figure, indicated a very poor cure.

The highest tensile figure shown in this comparison was 4800 pounds per square inch given by litharge.

The other oxides capable of bringing about rapid vulcanization were copper oxide, two other oxides of lead (Pb_3O_4 and PbO_2), and bismuth trioxide

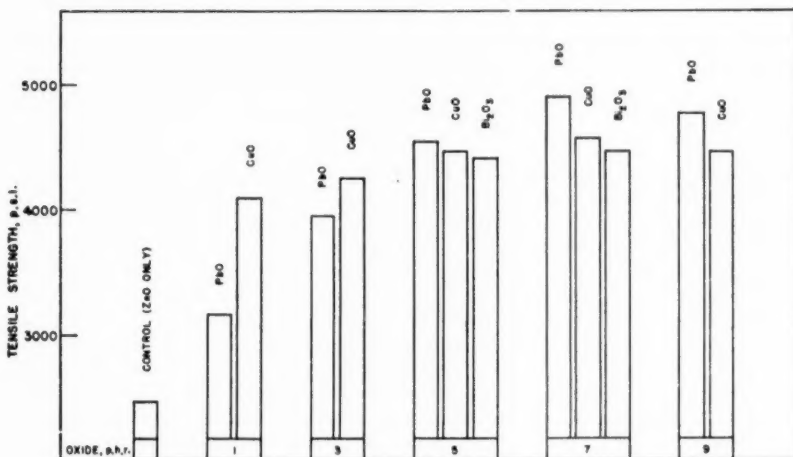


FIG. 3—Effect on tensile at best cure of varying quantities of oxide in lignin-natural rubber coprecipitate. Formulation 7: 27.8 volumes of lignin. All formulations contain 3 parts of zinc oxide per 100 parts of rubber.

(Bi_2O_3). Lead peroxide (PbO_2) was undercured in 10 minutes at 282°F , but the longer cures were satisfactory.

Varying the quantity of oxide.—Figure 3 shows the effect of varying the quantity of oxide. The tensile results for 1, 3, 5, 7, and 9 parts of oxide per 100 parts of rubber are shown. Formulation 7, Table III, which is the same as formulation 6 so far as zinc oxide, accelerator, and sulfur dosage are concerned, was used for this comparison.

Even 1 part of special oxide per 100 parts of rubber was effective. Copper oxide was effective in the lowest concentration, since with only 1 part per 100 parts of rubber a tensile strength of 4100 pounds per square inch was reached. The highest tensile strength (4900 pounds per square inch) was reached with 7 parts of litharge per 100 parts of rubber. Not much seemed to be gained by the use of quantities of oxide over 7 parts per 100 parts of rubber.

Certain organic accelerators, such as the lead, copper, and bismuth salts of dithiocarbamic acid derivatives, would provide a source of the three elements shown in the present study to be desirable for the vulcanization of lignin-natural rubber coprecipitates. These accelerators are available commercially, and when present in rubber in normal dosage, *i.e.*, 1 part per 100 parts of rubber,

TABLE II
FORMULATION 7, FOR DETERMINING THE EFFECT OF VARYING
QUANTITIES OF OXIDES (PARTS)

Natural rubber	72.2
Lignin, 27.8 vol. (coprecipitated)	36.1
Smoked sheet ^a	27.8
Stearic acid	2
Zinc oxide	3
Zinc dimethyldithiocarbamate	1
<i>N</i> -cyclohexyl-2-benzothiazole sulfenamide	0.5
Sulfur	2
Other metallic oxides (as shown in bar graphs)	1,3,5,7,9

^a Added to make rubber equal 100.

would provide the equivalent of about 0.4 part of bismuth oxide and about 0.2 part of copper or zinc oxide per 100 parts of rubber. These quantities are, however, lower than the optimum amount for satisfactory vulcanization.

AGING

The results of oven aging (2 days at 90°C) are given in Figure 4.

The rubber compounds were prepared according to formulations 8 to 12, inclusive, Table IV, and all contained 3 parts of zinc oxide per 100 parts of rubber with the exception of formulation 9, the lignin control, which contained 5 parts per 100 parts of rubber. The three special oxides tested in the lignin compounds were lead oxide, cupric oxide, and bismuth trioxide. The lignin control compound, just mentioned, contained only zinc oxide (5 parts per 100 parts of rubber). For purposes of comparison, a channel black tread formulation was placed in this series and had conventional acceleration, *i.e.*, *N*-cyclohexyl-2-benzothiazole sulfenamide, with 2.5 parts of sulfur per 100 parts of rubber. The lignin compounds had the same thiazole and dithiocarbamate acceleration as previous formulations, with 2 parts of sulfur and 7 parts of the various oxides per 100 parts of rubber as shown. The cures were 10, 20, 30, and 40 minutes at 282°F . Since cupric oxide compound was faster curing than the others, a shorter cure of 7.5 minutes was added and the 40-minute cure eliminated.

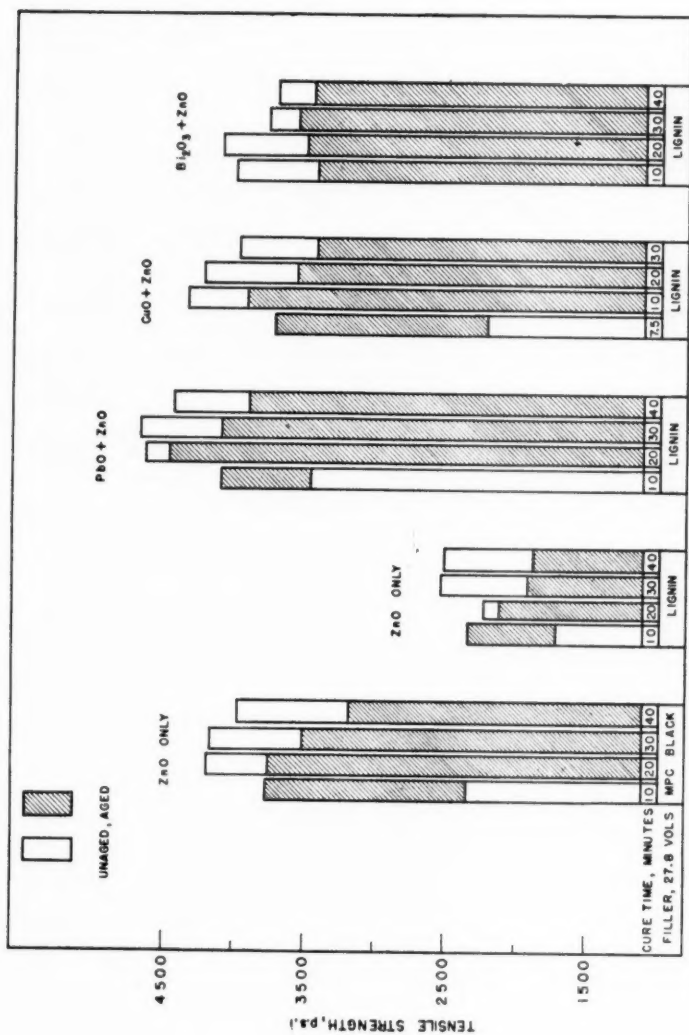


FIG. 4.—Comparison of oven-aged lignin-natural rubber coprecipitate with channel black tread compound. Formulations 8 through 12. All formulations contain zinc oxide; other oxides where present are in amounts of 7 parts per 100 parts of rubber.

TABLE IV
FORMULATIONS FOR AGING EXPERIMENTS AND RESULTS

	Formulation											
	8	9	10	11	12							
Natural rubber	—	72.2	72.2	72.2	72.2							
Lignin, 27.8 vol. (coprecipitated)	—	36.1	36.1	36.1	36.1							
Smoked sheet	100	27.8 ^a	27.8 ^a	27.8 ^a	27.8 ^a							
MPC black, 27.8 vol.	50	—	—	—	—							
Stearic acid	2	2	2	2	2							
<i>sym</i> -di- β -Naphthyl- <i>p</i> -phenyl-enediamine	2	2	2	2	2							
Pine tar	4	—	—	—	—							
Zinc oxide	3	5	3	3	3							
Lead oxide	—	—	7	—	—							
Cupric oxide	—	—	—	7	—							
Bismuth trioxide	—	—	—	—	—							
Zinc dimethyldithiocarbamate	—	1	1	1	1							
<i>N</i> -cyclohexyl-2-benzothiazole sulfenamide	—	—	—	—	—							
Sulfur	0.9	0.5	0.5	0.5	0.5							
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	—	—	—	—	—							
	—	—	—	—	—							
	—	—	—	—	—							
	—	—	—									

All the compounds contained 2 parts of symmetrical di- β -naphthyl-*p*-phenylenediamine antioxidant per 100 parts of rubber, since it was felt that an antioxidant is necessary for satisfactory aging.

The lignin compound, with zinc oxide only, had a relatively low tensile strength of around 2400 pounds per square inch before aging, which dropped to around 1900 pounds per square inch for the longer cures, after aging.

At the shortest cure all the compounds, except the lignin compound containing bismuth trioxide, increased in tensile strength after aging.

The litharge compound reached the highest tensile strength before and after aging. The unaged figure at the 30-minute cure of the litharge compound, for example, was around 4700 pounds per square inch, and the aged figure at the same cure was 4100 pounds per square inch. The best unaged and aged tensile figures for the channel black compound (20-minute cure) were 4200 and 3500 pounds per square inch, respectively. From the point of view of drop of tensile strength as well as actual tensile strength after aging, the litharge compound aged better than both the carbon black and the copper compound.

The bismuth compound had a somewhat lower unaged tensile strength than the channel black compound and the other lignin compounds containing the special oxides. However, with bismuth oxide in the formulation, the tensile strength was maintained at a high figure after aging, since the aged tensile at the 30- and 40-minute cure of the bismuth compound was better than that for the channel black compound at the same cures. On the basis of percentage drop of tensile strength on aging, at the longer cures, the bismuth compound appears to have shown the best aging characteristics of all the compounds tried.

The longest three cures of the cupric oxide compound showed noticeably better aged figures than the longest three channel black cures, and the cupric oxide unaged figures were either better than or equal to the corresponding channel black figures. The maximum drop of tensile strength of the cupric oxide compound upon aging was around 15 per cent while that of the channel black compound was around 20 per cent. Other physical characteristics of the copper compound, such as elongation at break, stress at 300 per cent elongation, and hardness, showed equally good aging (Table IV).

It is realized that copper is generally considered to be harmful to the aging of rubber, particularly natural rubber. In view of this, the aging experiments described above, were repeated. The repetition confirmed the results obtained.

Villain¹² found that among those materials that protect rubber against rapid aging because of copper are the accelerator and the antioxidant used in the lignin formulations in the present aging study. He also found that a typical copper inhibitor, disalicylaethylenediamine, needs an antioxidant, not necessarily a copper inhibitor, to bring about the maximum protective effect. Lignin-natural rubber masterbatch requires an antioxidant in the presence of, and in the absence of copper, but this antioxidant may be aldol α -naphthylamine which, according to Villain, does not have a specific anticopper effect. For example, formulation 11, Table IV, used in the aging tests, containing copper and dithiocarbamate, would have aged just as well if aldol- α -naphthylamine had been substituted for the copper-inhibiting *sym*-di- β -naphthyl-*p*-phenylenediamine.

Villain used the equivalent of 0.20 and 0.6 per cent of copper, calculated on the rubber, and observed serious aging in the absence of protection against copper, whereas in the aging tests described herein, the copper equivalent of the

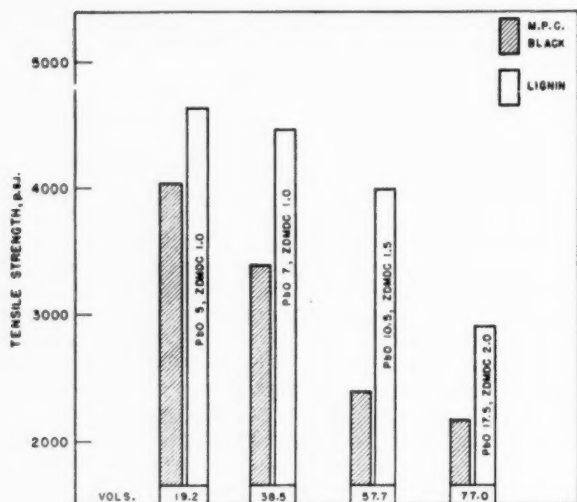


FIG. 5.—Comparison of tensile strength at best cure of lignin and channel black in natural rubber at equal volume loadings. Formulations 13 through 20.

TABLE V
FORMULATIONS FOR COMPARISON OF COPRECIPITATED LIGNIN
WITH CHANNEL BLACK AT VARIOUS LOADINGS

	Formulation			
	13	14	15	16
Smoked sheet	100	100	100	100
MPC black	34.6	69.3	104	138.5
Stearic acid	2	2	2	2
Pine tar	5	5	5	5
Zinc oxide	5	5	5	5
<i>N</i> -cyclohexyl-2-benzothiazole sulfenamide	0.7	0.7	0.7	0.7
Sulfur	2	2	2	2
Filler volume loading	19.2	38.5	57.7	77.0
Best tensile cure (min. at 282° F)	40	40	60	40

	Formulation			
	17	18	19	20
Natural rubber	100	100	100	100
Lignin (coprecipitated)	25	50	75	100
Stearic acid	2	2	2	2
Zinc oxide	3	3	3	3
Lead oxide	5	7	10.5	17.5
Zinc dimethyldithiocarbamate	1	1	1.5	2
<i>N</i> -cyclohexyl-2-benzothiazole sulfenamide	0.5	0.5	0.5	0.5
Sulfur	2	2	2	2
Filler volume loading	19.2	38.5	57.7	77.0
Best tensile cure (min. at 282° F)	20	30	20	20

copper oxide was 5.6 per cent on the rubber, or about 100 times the quantity used by Villain. The high copper content and the satisfactory aging of the lignin formulations indicate strongly that lignin is a copper inhibitor. However, a study of the possible anticopper properties of lignin does not come within the scope of the present investigation.

In view of the limited number of aging tests performed, it is probably not wise to recommend indiscriminate use of copper in lignin coprecipitate formulations. Nevertheless, in circumstances where contamination of rubber with copper during manufacture or in service has to be guarded against, it is thought that a lignin-coprecipitate formulation might be given consideration.

COMPARISON WITH CHANNEL BLACK

Tensile strength.—Figure 5 shows the result of a comparison of channel black with coprecipitated lignin at various loadings on the basis of tensile strength at best tensile cure.

Formulations 13 to 20, inclusive, Table V, were used. The channel black compounds had conventional thiazole acceleration. The special oxide in the lignin formulations in addition to zinc oxide was litharge, which was added in

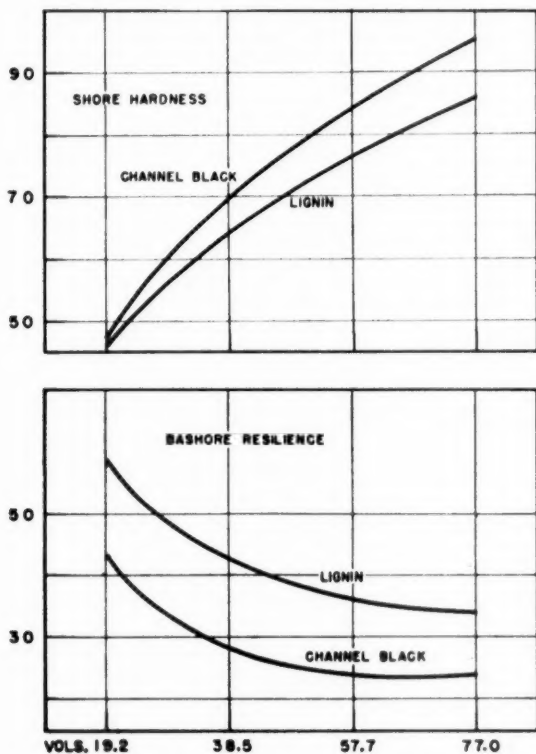


Fig. 6.—Shore hardness and Bashore resilience of lignin and channel black compounds at best tensile cure at various loadings. Lignin formulations contain lead oxide. Formulations 13 through 20.

the proportion of 5, 7, 10.5, and 17.5 parts by weight for lignin loadings of 19.2, 38.5, 57.7, and 77.0 volumes, respectively. The lignin formulations contained both thiocarbamate and thiazole acceleration. The thiocarbamate acceleration was increased for the higher loadings, *i.e.*, from 1 part, which was the dosage at the lower loadings, to 1.5 parts per 100 parts of rubber for the 57.7-volume loading and to 2 parts per 100 parts of rubber for the 77-volume loading.

The tensile strength of the lignin compound was considerably greater than that of the channel black compound at all loadings. The greatest difference

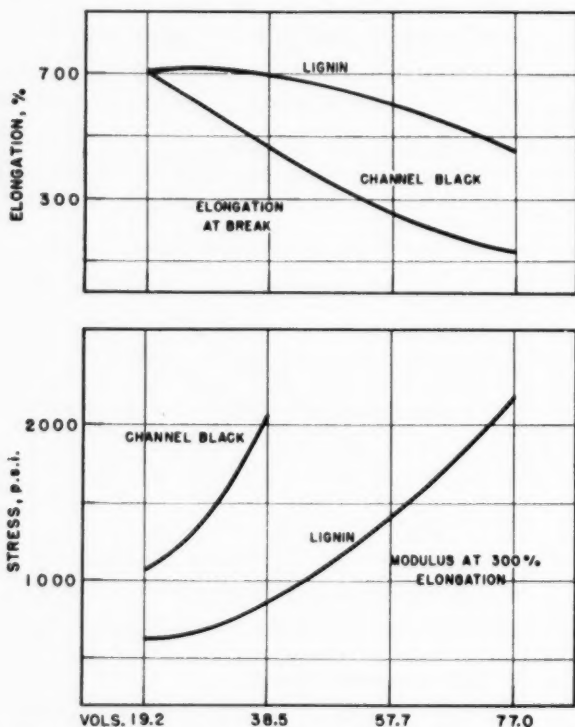


Fig. 7.—Elongation and modulus of lignin and channel black compounds at best tensile cure compared at equal loadings. Formulations 13 through 20. Lignin formulations contain lead oxide.

was at the 57.7-volume loading where the tensile strength of the lignin compound was 4000 pounds per square inch and that of the channel black compound was 2400 pounds per square inch.

Hardness and resilience.—Figure 6 shows a comparison of lignin and channel black on the basis of Shore hardness and Bashore resilience at the best tensile cure. The formulations were those just described, *i.e.*, 13 to 20, inclusive, Table V, and the tests were carried out on the same slabs as were used for the determination of tensile strength.

For equal volume loadings, the channel black compound is harder than the

lignin compound and the lignin compound is more resilient than the channel black compound.

The curves show that lignin is more resilient than channel black at equal hardness, as well as at equal volume loading. At a hardness of 70, for example, the resilience of lignin is about 38, whereas at this hardness channel black has a resilience of only 28.

Elongation and modulus at 300 per cent.—Elongation at break and modulus at 300 per cent were also observed for compounds made from formulations 13 to 20, inclusive. Figures obtained at the best tensile cure are shown in Figure 7.

The lignin compounds had a considerably higher elongation at break than the channel black compounds at equal loadings and the channel black a considerably higher modulus at 300 per cent elongation.

MOONEY SCORCH

Table VI shows the Mooney scorch figures for the various oxides compounded according to formulation 6. These compounds had 3 parts of zinc oxide plus 7 parts of additional special oxide per 100 parts of rubber, with the

TABLE VI

Metallic oxide	Mooney scorch (min. to 4-point rise, MS units, 250° F)
ZnO + CuO	35
ZnO + Bi ₂ O ₃	35

exception of the control, which had only 3 parts of zinc oxide per 100 parts of rubber.

It is interesting to note that the control, which did not cure too well, was slightly more scorchy by a few minutes than the compounds containing zinc oxide plus cupric oxide, and zinc oxide plus bismuth oxide.

The compound containing litharge was the most scorchy, but if considered necessary, this could be corrected by adjustment of accelerator or special oxide.

COST OF OXIDES

The prohibitive price of bismuth oxide at around \$4.50 per pound should be noted. Litharge costs around 22 cents per pound, zinc oxide around 20 cents. Copper oxide is still competitive at around 40 cents per pound because it is effective in lower dosages.

These are rough quotations taken from the current literature.

CONCLUSION

Although the experiments recorded herein are strictly of a compounding nature, nevertheless it is believed that they have made contributions to the knowledge of the chemistry of vulcanization. The most probable explanation of the delaying effect of lignin on vulcanization is that it reacts too readily with sulfur during vulcanization and thus builds up an excessive hydrogen sulfide concentration. There are metals whose oxides can control the hydrogen sulfide concentration to the proper degree during the vulcanization of lignin-natural rubber coprecipitates; such oxides are those of lead, copper, and bismuth.

SUMMARY

No difficulty is experienced in the vulcanization of natural rubber containing lignin added as a dry powder, but this method of addition results in relatively low tensile strengths. When lignin solution was added to latex, however, the masterbatch obtained by coprecipitation was difficult to vulcanize. For example, if conventional acceleration was used, *i.e.*, mercaptobenzothiazole with zinc oxide, the test slabs were soft, tacky, and logy, and could be removed from the mold only with difficulty. Although hydrogen sulfide might be a necessary intermediate in the vulcanization reaction, published experimental evidence shows that an excessive concentration of hydrogen sulfide retards vulcanization, even in the presence of powerful organic accelerators.

In order to test the possibility that the retardation of cure with lignin master batches might be due to excessive hydrogen sulfide developed during vulcanization, owing to reaction of sulfur with lignin, various metallic oxides were tried which might react with hydrogen sulfide to form insoluble sulfide, and so reduce the hydrogen sulfide concentration. Lead oxides, copper oxide, and bismuth oxide were successful with lignin masterbatches, particularly when used with a dithiocarbamate accelerator. A lignin compound containing litharge, curing in 20 minutes at 282° F, had a tensile strength about 800 pounds per square inch above that obtainable with MPC carbon black. The Bashore resilience figure for the lignin compound was about double that for MPC carbon black.

The aging qualities of vulcanizates containing lead oxide and lignin appear to be good, and even copper oxide, which is normally considered to be detrimental, ages satisfactorily, provided an antioxidant is included. A lignin compound containing 7 parts of copper oxide on 100 parts of rubber and 2 parts of antioxidant showed a drop of less than 20 per cent of its tensile strength after 2 days in an air oven at 90° C.

ACKNOWLEDGMENT

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EFFECT OF SEVERITY OF SERVICE ON THE RELATIVE ABRASION RESISTANCE OF NATURAL RUBBER, GR-S-10, AND GR-S-100 *

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A large number of test devices has been utilized by the rubber industry to measure the abrasion resistance of rubber compounds. Correlation of laboratory data with service performance is difficult because of the large number of factors which influence abrasion, and during the past ten years the problem of correlation has become even more acute owing to the wide acceptance of synthetic elastomers.

It is known that the rate at which rubber is abraded, both in laboratory tests and in service, is determined by the severity of the test conditions. Some of the factors which affect the rate of wear of tires are wheel load, tire position, condition of road surface, atmospheric temperature, mechanical condition of the vehicle, and driver practices. The important factors in a laboratory abrasion test are the load on the specimen, angle of contact, type of abrasive surface, atmospheric temperature, and test-specimen temperature.

The influence of different operating conditions has been investigated quite extensively in this laboratory, using the modified Goodyear angle abrader¹. This work was conducted with tread stocks for which road performance had been determined in order to establish operating conditions which would simulate actual tire wear.

The relative abrasion resistance ratings of different stocks were affected by the severity of the test conditions, both in the laboratory and road tests. It is the purpose of this report to show the effect of test severity on the relative ratings of natural rubber, GR-S-10 (122° F non-pigmented polymer) and GR-S-100 (41° F non-pigmented polymer) tread compounds.

SCOPE OF DATA

The tire test data in this report were obtained from eight different tire tests conducted under both closely and partially controlled conditions. All the tires for which results are cited were prepared by the same manufacturers, and were identical in size (7:00 X 15), tread design, and tread formulations. The tread compounds were natural rubber, GR-S-10, and GR-S-100. The natural rubber stock was a conventional compound containing EPC black; both of the synthetics were compounded with HAF black.

The tires in the first four tests are identical, and the road tests were conducted at approximately the same time. The tires in the last four tests were made and tested at different times.

The laboratory abrasion tests were conducted on factory mixed tread compounds which were similar to the road tested stocks. The stocks were tested on the modified Goodyear angle abrader at varying degrees of severity. The severity was controlled by varying the wheel angle.

* Reprinted from the *India Rubber World*, Vol. 127, No. 3, pages 363-364, December 1952.

TABLE 1
ROAD WEAR ABRASION RESULTS

Rubber	Miles	Miles 0.001" tread loss	Abrasion index (%)
		Test No. 1	
Natural	8901	23.6	100
GR-S-100	8901	50.9	216
GR-S-10	8901	46.4	197
		Test No. 2	
Natural	17780	43.4	100
GR-S-100	17780	66.1	153
		Test No. 3	
Natural	29900	109.1	100
GR-S-100	29900	120.2	111
GR-S-10	29900	101.7	94
		Test No. 4	
Natural	43130	142.5	100
GR-S-100	43130	140.3	98
		Test No. 5	
Natural	30221	74.2	100
GR-S-100	30221	106.8	144
		Test No. 6	
Natural	13197	43.0	100
GR-S-100	13197	71.1	164
		Test No. 7	
Natural	19980	61.8	100
GR-S-100	19980	99.4	161
GR-S-10	19980	72.4	117
		Test No. 8	
Natural	11812	41.3	100
GR-S-100	11812	74.3	179
GR-S-10	11812	62.3	151

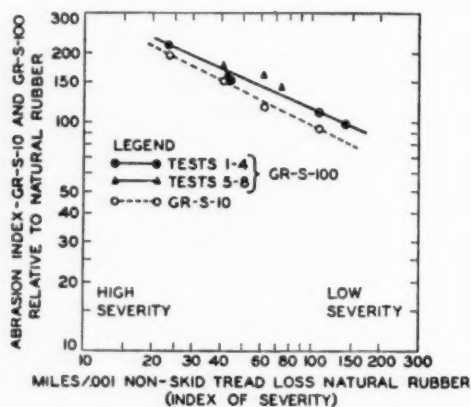


Fig. 1.—Effect of severity on abrasion index of GR-S-10 and GR-S-100—road test data.

TABLE 2
LABORATORY ABRASION RESULTS

Rubber	Abrasion wheel angle (degrees)						
	5	8	10	12	14	17	20
	Grams loss						
Natural	0.17	1.39	3.59	6.73	9.52	15.23	18.85
GR-S-100	0.25	1.27	2.55	4.04	5.76	7.14	7.71
GR-S-10	0.16	1.07	2.52	4.68	6.62	8.57	8.68
	Abrasion index						
Natural	100%	100%	100%	100%	100%	100%	100%
GR-S-100	68	109	141	167	165	213	244
GR-S-10	106	130	142	144	144	178	217

TABLE 3
300 PER CENT MODULUS OF RUBBERS IN TIRE TESTS 1-4

Minutes cure at 307° F	Original		Aged 24 hours at 212° F	
	30	45	30	45
Natural rubber	930	950	1370	1350
GR-S-100	1120	1380	2850	2810
GR-S-10	950	1200	—	2520

ARRANGEMENT OF DATA

The miles, miles per thousandth inch non-skid tread loss, and abrasion index values for all eight tire tests are shown in Table 1. Laboratory abrasion results determined at 5, 8, 10, 12, 14, 17, and 20 degrees wheel angles for similar tread stocks are presented in Table 2.

In Figure 1 the relative ratings of GR-S-10 and GR-S-100 in road tests, compared to natural rubber pegged at 100 per cent in each test, are shown as a function of the severity. The miles per thousandth inch nonskid tread loss of the natural rubber control in each test has been used as the index of severity; a high value of miles per thousandth inch nonskid loss indicates relatively light service; while a low value indicates very severe service. The relative ratings based on laboratory abrasion results for GR-S-100 and GR-S-10, compared to

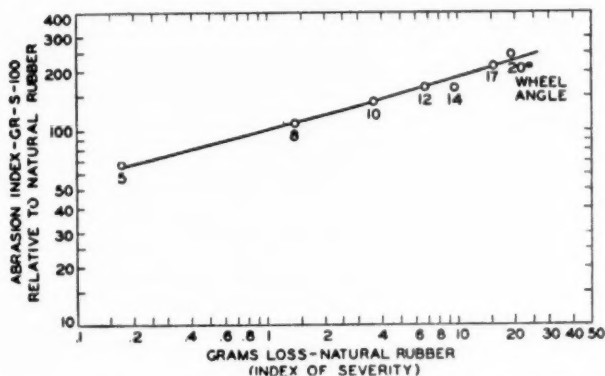


Fig. 2.—Effect of severity on abrasion index of GR-S-100—laboratory abrasion data.

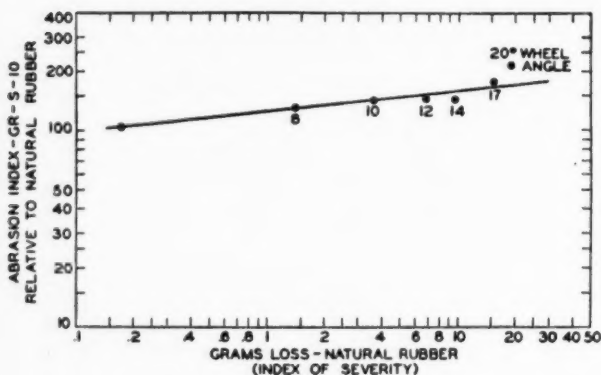


Fig. 3.—Effect of severity on abrasion index of GR-S-10—laboratory abrasion data.

natural rubber pegged at 100 per cent at each test condition, are shown in Figures 2 and 3, respectively. The weight loss of the natural rubber compound is used as an index of severity; a small loss designates light service; while a large loss designates severe test conditions.

DISCUSSION OF RESULTS

The data show that as the severity of both the laboratory and road tests was increased, the relative abrasion resistance ratings of GR-S-10 and GR-S-100 were increased.

Compared to natural rubber pegged at 100 per cent the abrasion index of GR-S-100 increased from 98 per cent in light service to 216 per cent in very severe service. In a similar manner the laboratory abrasion data show that the abrasion rating of GR-S-100 increased from 68 per cent at a five-degree wheel angle to 244 per cent at a 20-degree wheel angle.

The relative rating of GR-S-10 varied from 94 per cent in light service to 197 per cent in very severe service road tests. A similar relation is seen in the laboratory test data.

CONCLUSIONS

The data in this report show that the rate of wear is affected very greatly by the severity of the test. Both laboratory and actual road wear performance data show that synthetic rubber and natural rubber are fairly similar in rate of wear under mild conditions of testing, but in severe service the synthetic polymers are vastly superior to natural rubber. It therefore becomes evident that, in order to correlate laboratory data with road test results, the severity of service must be known, and a laboratory test conducted under one set of conditions would not necessarily be expected to correlate with all road test results.

ACKNOWLEDGMENT

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DIRECT DETERMINATION OF OXYGEN IN RUBBER

COMPARISON BETWEEN ISOTOPIC AND SCHÜTZE- UNTERZAUCHER METHODS *

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In the past, oxygen has been determined in rubber, as in other organic compounds, by difference¹. This method was time-consuming and was subject to cumulative errors. Only in the past twenty-five years have serious attempts been made to develop a direct analytical method for the determination of oxygen. The first successful attempt was by ter Meulen², who catalytically hydrogenated the oxygen of organic materials to water. Cramer, Sjöthun, and Oneacre³ applied ter Meulen's method of determining oxygen to rubber. This method has the disadvantage of most catalytic methods, in that it requires careful and accurate control and purity of the catalyst. In 1939 a more convenient method was developed by Schütze⁴ and later improved by Unterzaucher⁵. This method is based on the decomposition of the organic compound in a stream of pure nitrogen over pure carbon at a temperature of 1120° C. All of the oxygen of the organic compound appears as carbon monoxide. Chambers⁶ and Walton, McCulloch, and Smith⁷ used this method to determine the oxygen content of rubber. An excellent review by Elving and Ligett⁸ summarizes these methods of analyzing for oxygen in organic compounds.

All the above-mentioned methods require quantitative separation and quantitative recovery of the oxygen-containing compound or of its reaction products. In 1946 Grosse, Hindin, and Kirshenbaum⁹ developed an isotopic method for determining the oxygen content of organic compounds. The isotopic method has the fundamental advantage that quantitative results are obtained without any quantitative separation or recovery of any oxygen or oxygen-containing compounds. In this paper the isotopic method is compared directly with the Schütze-Unterzaucher method for determining oxygen in rubber.

SCHÜTZE-UNTERZAUCHER METHOD

The sample is vaporized at 950° to 1000° C in a stream of pure nitrogen, and the products are carried over carbon heated at 1100° to 1150° C, whereby all the oxygen present is converted to carbon monoxide. The latter is then oxidized to carbon dioxide by iodine pentoxide, and the equivalent amount of iodine liberated is determined titrimetrically with sodium thiosulfate. This method has been described in detail in other publications¹⁰.

The rubber sample (30 to 50 mg.) is vaporized at 1000° \pm 25° C in a stream of nitrogen (10 cc. per minute) and passed over carbon heated at 1150° \pm 25° C in a quartz reaction vessel. The carbon monoxide formed is swept by nitrogen over pure iodine pentoxide heated to 120° C, and thus converted to carbon

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dioxide. Simultaneously, the iodine pentoxide is reduced to iodine, which is determined quantitatively by titrating with a standard solution of 0.02 *N* sodium thiosulfate. The nitrogen used is first freed of all traces of oxygen by passing the gas over copper heated at 500° C.

ISOTOPIC METHOD

The principle of the isotopic method is an adaptation of the isotopic dilution principle originally introduced by von Hevesy and Paneth¹¹. The sample, together with a known amount of oxygen-18 is heated in a platinum tube to the point of decomposition (800° to 900° C) for 30 to 60 minutes. At this temperature all the oxygen atoms exchange statistically with the various oxygen-containing compounds which are stable at these temperatures (water, carbon dioxide, carbon monoxide, oxygen, and any oxygen in the residue). The ratio of the oxygen isotopes in all of these compounds is identical. The ratio, oxygen-18 to oxygen-16, of a small sample of the gas is determined with a high degree of precision by means of modern isotopic mass spectrometers. Knowing the ratio one can easily calculate the original oxygen content from the simple mixture rule, for which the equation is:

$$x\% = \frac{b(m - n)}{an} \times 100$$

where *a* is the known weight of the sample to be analyzed, containing *x* weight-% oxygen and is equilibrated with a known weight, *b*, of oxygen-18-labeled oxygen, containing *m* atom-% of oxygen-18 in excess of normal isotopic concentration (~0.21 atom-%), and where *n* atom-% is the excess oxygen-18 concentration after equilibration. This method is described in great detail in previous publications¹².

A detailed description of the apparatus is given by Grosse, Hindin, and Kirshenbaum⁹, while the present equipment used at the Research Institute together with the most accurate results appeared previously¹³. The experimental procedure is the same as previously described except for a few minor changes in sample introduction and in concentration of carbon dioxide for mass spectrometer analysis. The rubber samples were weighed in a platinum boat and inserted into the platinum combustion tube; the latter was then sealed to the vacuum system by means of a Hoke needle valve and glass-to-copper seal.

When rubber containing small amounts of oxygen was combusted with oxygen-18 enriched-oxygen gas, the gases formed contained water, methane, ethane, and small amounts of carbon monoxide and carbon dioxide. To determine the percentage oxygen in the rubber, the oxygen-18 to oxygen-16 ratio of the oxygen in either the carbon dioxide or the carbon monoxide, preferably that in the carbon dioxide, has to be determined. This is so because the presence of nitrogen gives low ratios of oxygen-18 to oxygen-16 in the carbon monoxide (high oxygen values in the rubber), since both carbon monoxide and nitrogen each give 28 mass peaks on the mass spectrometer. For the greatest accuracy, the carbon dioxide concentration in the gas analyzed on the mass spectrometer should be as high as possible. In order to concentrate the carbon dioxide, the gases were passed through a liquid nitrogen trap, and the noncondensable gases (carbon monoxide, hydrogen, and methane) were evacuated, leaving the condensable gases (carbon dioxide, methane, and ethane), behind in the liquid nitrogen trap. To concentrate the carbon dioxide further, the condensable gases were warmed from -195° to -145° C by replacing the liquid nitrogen

TABLE I
DETERMINATION OF OXYGEN CONTENT OF SMOKE SHEET RUBBER BY ISOTOPIC METHOD AND UTTERZAUCHER METHOD

Sample	State of oxidation	By isotopic method				By Uterzaucher method Observed % oxygen	Difference, Av. % oxygen (I-U)	% Oxygen, calculated by "Gain in weight" ^a	
		a, Wt. of sample (mg.)	b, Wt. of oxygen-18 gas (mg.)	m in b	n in equi- brated mixture			Gain	Total
1	Unoxidized	418.62	5.50	5.1080	1.7932	2.46		1.20	0
		409.77	6.69	5.5795	2.0657	2.42		1.38	
		424.24	6.35	5.0795	1.8606	2.59		—	
2	30 hours in O ₂ bomb at 70° C, Oxidation 1	418.42	6.89	5.0795	1.9973	2.55		—	1.21
		313.54	4.49	5.0795	1.9239	2.43		1.29±0.09	
		326.59	4.27	5.0795	1.8114	2.45		2.13	
3	30 hours in O ₂ bomb at 70° C, Oxidation 2 at Lee Rubber & Tire Co. ^b	351.54	7.04	5.1080	1.7932	2.45		2.44	0.16
		352.78	4.99	5.0795	1.8357	2.27		2.28±0.16	
		328.34	4.23	5.0795	1.8287	2.50		0.85	
4	195 hours in O ₂ bomb at 70° C (Sample 3 oxi- dized for additional 165 hours)	235.42	4.11	5.0795	1.5401	2.36		—	0
		447.65	7.53	5.0795	1.5429	2.38		0.89±0.04	
		314.60	6.99	5.0795	1.6433	4.04		3.62	
5	218 hours in O ₂ bomb at 70° C (Sample 3 oxi- dized for additional 188 hours)	415.73	7.39	5.0795	1.3892	4.14		3.41	1.74
		303.23	4.53	5.1080	1.0388	4.09		3.41	
		303.23	4.53	5.1080	1.0388	4.09±0.05		3.52±0.11	
6	30 hours in O ₂ bomb at 70° C (Sample 3) + 64 hours at 82.5° C	314.60	6.99	5.0795	1.6433	4.66		3.42	2.48
		415.73	7.39	5.0795	1.3892	4.82		3.80	
		303.23	4.53	5.1080	1.0388	4.74±0.08		3.61±0.19	
	Sample melted ^b	452				5.88		4.52	Sample melted ^b
		469				4.69		4.69	
		4.61±0.08						1.27	
								Av. 0.95	

^a % Oxygen by "Gain in weight" calculated by adding the weight gain upon heating in O₂ to the values obtained by isotopic method for samples 1 and 3.

^b No gain in weight obtained.

trap by a melting isobutane bath (melting point = -145°C). On warming to -145°C , the organic gases (methane and ethane) were pumped off at a pressure not below 1 to 2 mm., leaving behind highly concentrated carbon dioxide, since the vapor pressure of carbon dioxide is only 0.24 mm. at -145°C .

EXPERIMENTAL RESULTS

The rubber samples analyzed were smoked sheet rubber in various stages of oxidation. Whenever possible, the changes in weight of the rubber upon oxidation in the oxygen bomb were recorded.

The results obtained by the isotopic method for the rubber samples oxidized in the oxygen bomb are given in Table I. The reproducibility by this method is very good.

Samples of the same six rubbers analyzed by the isotopic method were also analyzed by the Schütze-Unterzaucher method at the microchemistry laboratory of Carl Tiedeke in Teaneck, N. J. A comparison of these results with those obtained by the isotopic method is shown in Table I. It can be seen from this comparison that the values obtained by the Unterzaucher method as practiced at the Tiedeke Laboratories are always lower than those obtained by the isotopic method. The differences are between 7 to 50 per cent below the isotopic values. The authors believe that this is due to inherent inaccuracies in the Schütze-Unterzaucher method as discussed later.

In order to determine whether the isotopic values were high or the Unterzaucher values were low, these values were compared with those calculated from "gain in weight". This comparison is shown in Table I, and it assumes that the isotopic values are the correct ones for the unoxidized samples and 30-hour oxidation samples. It can be seen from this comparison that the isotopic values agree very nicely with the "gain in weight" values, being only 0.03 to 0.14 per cent lower, while the Unterzaucher values are from 0.3 to 1.5 per cent lower (1.2 to 62 per cent of actual oxygen values). If the Unterzaucher values for the unoxidized and 30-hour-oxidized samples were assumed to be the correct ones, then the differences between the "gain in weight" values and the Unterzaucher values would be still greater, the error being positive. Thus the Unterzaucher values are low. These low results can be explained by subjecting the principle of this method to closer scrutiny.

In the Unterzaucher method the compound analyzed is vaporized and decomposed over hot carbon. Some compounds, however, do not vaporize or gasify completely—for example, sucrose leaves a carbonaceous residue, while rubber leaves a deposit on the carbon. Both the residue and the deposit may contain oxygen which cannot be taken into account by the Unterzaucher method. The same holds true for the ter Meulen method. The proof that these deposits and residues contain oxygen is given in the following experiments.

A stream of oxygen-free nitrogen was passed for 3 hours over 2.950 grams of sucrose heated at 1150°C , and then for 1 hour while cooling to room temperature. A residue, corresponding to 11.0 weight-% of the sucrose, remained. This residue, when analyzed for oxygen by the isotopic method, gave 2.18 weight-% oxygen, which equals 0.23 weight-% of the original sucrose.

A 0.6736-gram sample of smoked sheet rubber oxidized in the oxygen bomb for 30 hours at 70°C (containing 2.44 weight-% oxygen) was vaporized in an oxygen-free nitrogen stream and passed over carbon heated at $1150^{\circ} \pm 25^{\circ}\text{C}$. The carbon after use weighed 2.170 grams. Samples of both the unused and used carbon were analyzed for oxygen by the isotopic method. The unused

carbon was found to contain 0.195 weight-% oxygen while the used carbon contained 0.345 weight-%. Thus the carbon gained 0.151 weight-% oxygen or 3.28 mg. of oxygen. This 3.28 mg. corresponds to 0.49 weight-% oxygen of the rubber used.

This difficulty is not encountered with the isotopic method, because of its very nature. In the isotopic method the oxygen-18 of the oxygen added exchanges statistically with the oxygen-16 in all the decomposition products of the rubber (carbon monoxide, carbon dioxide, water, and oxygen-containing char), resulting in all of these oxygen-containing compounds having identical oxygen isotope ratios. It was demonstrated experimentally¹², in the case of hydrocarbon derivatives, that complete equilibrium is established in less than half an hour at red heat. As a further illustration, the oxygen content of water can be exchanged quantitatively with oxygen-18-labeled oxygen gas even at room temperature, in the presence of platinum, under conditions where neither the water nor the oxygen molecule undergoes any decomposition.

SUMMARY

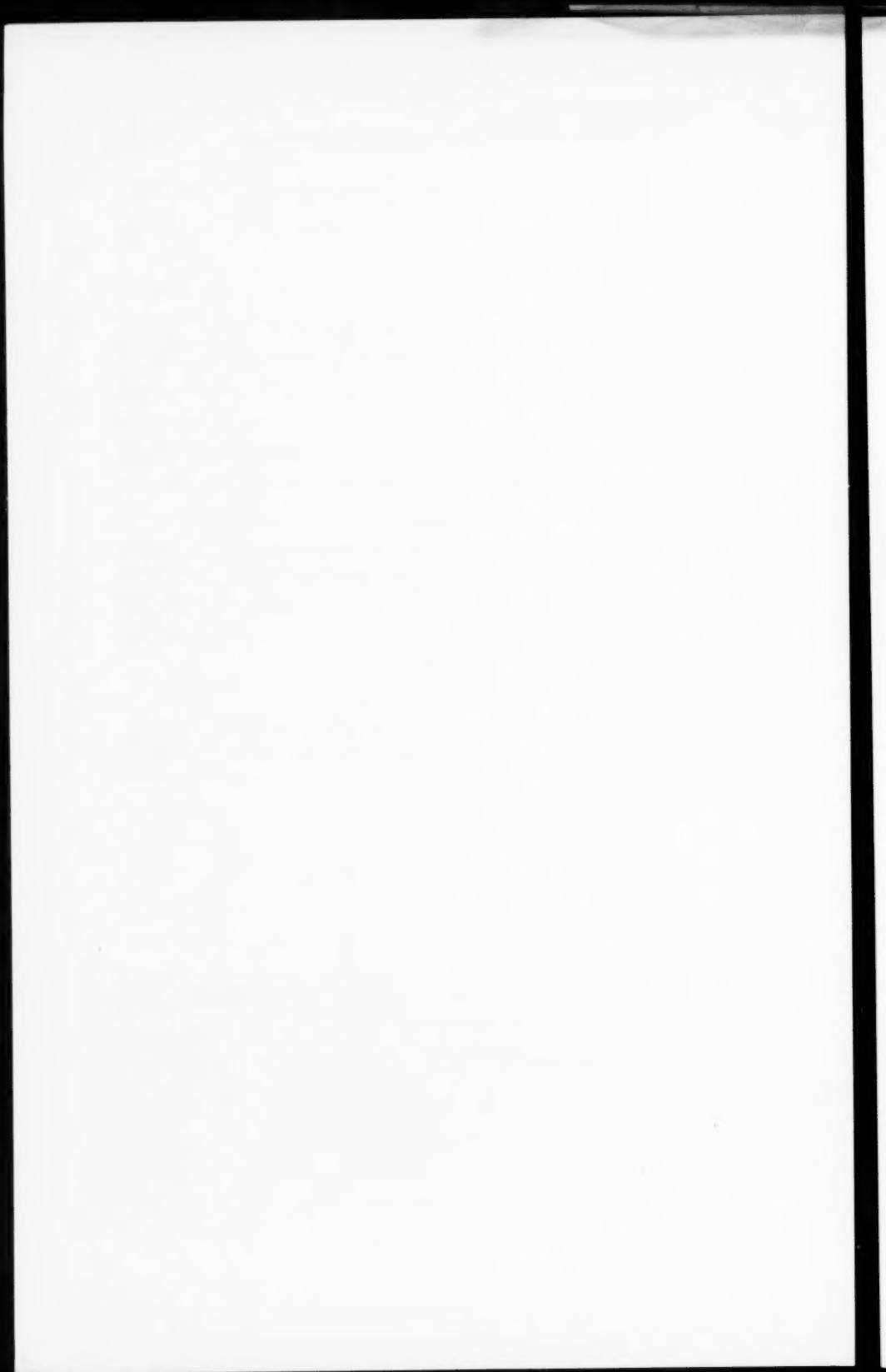
The values obtained by the isotope method for the direct determination of oxygen in rubber agree very nicely with the values obtained for the gain in weight on oxidation. The values obtained by the Schütze-Unterzaucher method, reported herein, are all low. This study indicates that the Schütze-Unterzaucher may give low oxygen values for compounds which form non-vaporizable carbon residues, such as rubber.

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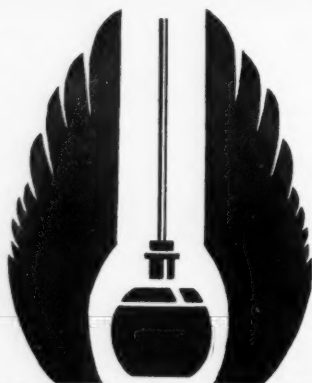


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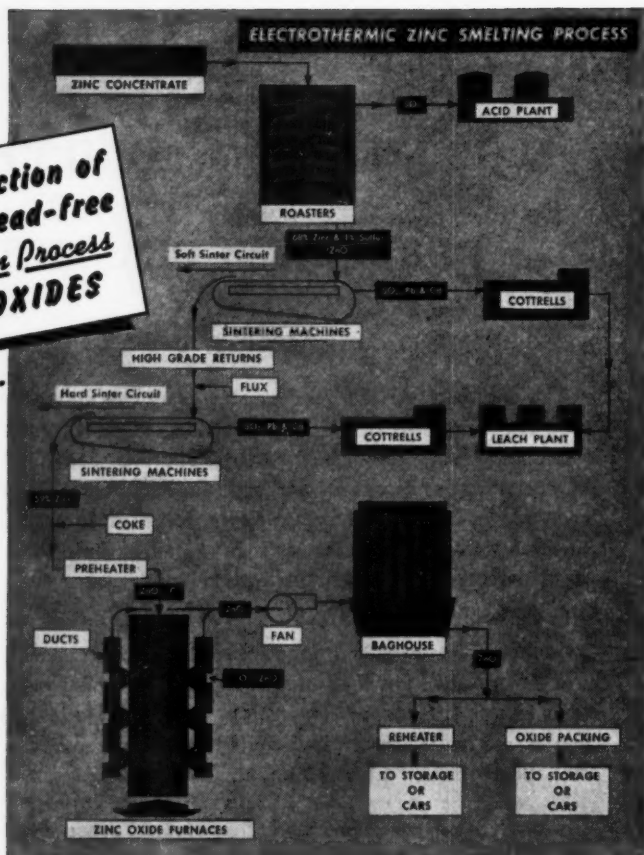
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